RESEARCH DATA RELATING TO THE DEVELOPMENT OF DURABLE PRESS COTTON FABRICS BY VAPOR PHASE TECHNIQUES

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RESEARCH DATA RELATING TO THE DEVELOPMENT OF DURABLE PRESS COTTON FABRICS BY VAPOR PHASE TECHNIQUES

by

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INTRODUCTION

The data and information presented herein represent re-arranged excerpts from eight quarterly technical reports of the Gagliardi Research Corporation on work done under Contract No. 12-14-100-7177(72) for the Southern Utilization Research and Development Division, Agricultural Research Service, United States Department of Agriculture. These excerpts are restricted to those sections which chronologically show vapor phase studies on the crosslinking of cotton and the evolution of a vapor phase durable press process for the treatment of cotton garments. Summaries of all the above vapor phase reactions have been given in the following publications:

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New Orleans, Louisiana

1. "Vapor-Phase Reactions on Cotton, Part I, General Considerations and Partial Results" Textile Res. J., 36, No. 2, pp. 168-77 (1966).
2. "Vapor Phase Reactions on Cotton, Part II, Vapor Phase Permanent Press Process," to be published in Textile Research J. Preprints are available of this paper as presented at the 1966 Meeting of the Textile Research Institute.
3. "Vapor Phase Grafting and Its Relation to Permanent Press," paper presented at Sixth Cotton Utilization Research Conference in New Orleans, La., on April 22, 1966.

CROSSLINKING WITH FORMALDEHYDE VAPORS AND CATALYSIS

Vapor phase reactions of formaldehyde with cotton have established clearly that practical crosslinking processes might be devised for the commercial treatment of fabrics. For those aldehyde reactions where HCl might not be desirable as a catalyst, other techniques would have to be employed, e.g., preimpregnation with suitable nonvolatile catalyst.

In Table 1 are shown some preliminary tests with different sources of formaldehyde. Since the partial vapor pressure of formaldehyde varies widely with the solvent and since formaldehyde is known to form a variety of azeotropes with water and alcohols (see Walker "Formaldehyde" ACS Monograph No. 159), it was expected that some forms might be more desirable in one experiment and not in another. Aqueous and methanolic formaldehyde solutions yield the higher weight gain. Attempts to increase the yield of combined formaldehyde by increasing the HCl concentration result in completely degraded fabrics.

TABLE 1.--Weight gain produced from various formaldehyde sources from 2 days' exposures at 21° C. - 10 g. contained formaldehyde; 25 ml. conc. HCl

Formaldehyde Source	% Weight Gain Initial
91% p-CH_2O	-0.3
40% Butyl Formcel	0.1
55% Methyl Formcel	0.6
37% Aqueous CH_2O	2.9

Paraformaldehyde

In Table 2 are shown tests done with paraformaldehyde and a variety of preimpregnated catalysts. These were applied from aqueous solutions and dried at low temperatures, 5/220°F. Then the samples were exposed to the vapors of paraformaldehyde. The weight gain produced is extremely small even after 14 days exposure, indicating either insufficient formaldehyde vapors or deficient catalysis. These experiments were repeated for the one and seven day periods. One half of each sample was heated for 10 minutes at 300°F. after the exposure and before scouring. Because of the small weight gains involved, we measured crease resistance by the Monsanto Tester and also tested the samples for immunization against dyeing with the direct dye Fastusol Blue LBRRA (C.I. Direct Blue No. 71). The results are shown in Table 3. The vapor exposure alone produces no immunization against dyeing, nor does it yield crease resistance. When the seven days samples were heated, however, high crease resistance was produced by four of the catalysts indicating that sufficient amounts of formaldehyde have been absorbed by the fibers.

In Table 4 are shown further repetitions of the paraformaldehyde experiments but at higher temperatures for 24 hours. The weight gain test was not sensitive enough to indicate fiber reaction. Note that at 80° C., high crease resistance is obtained, especially with ammonium chloride and cupric chloride.

TABLE 2.--91% p-CH_2O vapors on cotton preimpregnated with acidic catalysis (21°C. exposures)

Catalyst Applied - 1%	Exposure Time - Days	% Weight Gain	
		Initial	Fixed
$MgCl_2.6H_2O$	1	0.4	-0.1
$MgCl_2.6H_2O$	7	0.8	-0.1
$MgCl_2.6H_2O$	14	0.8	0.2
$Zn(BF_4)_2.7H_2O$	1	0.1	-0.2
$Zn(BF_4)_2.7H_2O$	7	1.2	-0.1
$Zn(BF_4)_2.7H_2O$	14	1.1	0.1
$CuCl_2.2H_2O$	1	0.2	0.0
$CuCl_2.2H_2O$	7	0.8	0.2
$CuCl_2.2H_2O$	14	0.7	0.4
$Zn(NO_3)_2.6H_2O$	1	0.1	-0.1
$Zn(NO_3)_2.6H_2O$	7	0.7	-0.1
$Zn(NO_3)_2.6H_2O$	14	0.8	0.3
NH_4Cl	1	0.3	-0.4
NH_4Cl	7	0.5	-0.4
NH_4Cl	14	0.6	0.2

TABLE 3.--91% p-CH_2O vapors on cotton preimpregnated with acidic catalysts (21°C. exposure)

Catalyst applied-%	Exposure time days	Dye Test[1/] vapors only	Dye Test[1/] Plus cure	Crease Recovery Angle-Warp Vapors only	Crease Recovery Angle-Warp Plus cure
$MgCl_2 \cdot 6H_2O$	1	-	-	85	88
$MgCl_2 \cdot 6H_2O$	7	-	+	85	131
$Zn(BF_4)_2 \cdot 7H_2O$	1	-	-	85	89
$Zn(BF_4)_2 \cdot 7H_2O$	7	-	+	85	101
$CuCl_2 \cdot 2H_2O$	1	-	-	85	90
$CuCl_2 \cdot 2H_2O$	7	-	+	85	135
$Zn(NO_3)_2 \cdot 6H_2O$	1	-	-	85	87
$Zn(NO_3)_2 \cdot 6H_2O$	7	-	+	85	135
NH_4Cl	1	-	-	85	90
NH_4Cl	7	-	+	85	133

[1/] (-) no immunization against dyeing; (+) immunized --little or no dyeing.

TABLE 4.--91% p-CH_2O vapors on cotton preimpregnated with acidic catalysts (24 hours exposure)

Catalyst applied	Exposure Temperature	% Weight Gain Initial	% Weight Gain Fixed	Warp crease recovery angle
$MgCl_2.6H_2O$	50° C.	-0.2	-0.9	76
$MgCl_2.6H_2O$	80° C.	0.4	0.0	114
$Zn(BF_4)_2.7H_2O$	50° C.	-0.6	-0.7	76
$Zn(BF_4)_2.7H_2O$	80° C.	0.0	0.0	110
$CuCl_2.2H_2O$	50° C.	-0.2	-0.7	72
$CuCl_2.2H_2O$	80° C.	0.2	-0.2	142
$Zn(NO_3)_2.6H_2O$	50° C.	-0.4	-0.6	79
$Zn(NO_3)_2.6H_2O$	80° C.	0.2	-0.2	118
NH_4Cl	50° C.	-0.2	-0.7	134
NH_4Cl	80° C.	-0.5	-0.4	153
Untreated Control	-	-	-	75

In Table 5 a similar experiment is shown using the 55% methyl formcel. Again the NH_4Cl and $CuCl_2.2H_2O$ yield the higher crease resistance. Note, however, that with the methyl formcel there is a measurable weight gain produced as compared with the paraformaldehyde experiment. The two stated catalysts appear to be highly suited for vapor phase aldehyde reactions.

TABLE 5.--Methyl Formcel vapors on cotton preimpregnated with acidic catalysts

[24 hours exposure]

Catalyst applied - 1Percent	Exposure temperature	Percent weight Gain Initial	Percent weight Gain Fixed	Warp crease recovery Angle
$MgCl_2.6H_2O$	50° C.	1.2	0.0	82
$MgCl_2.6H_2O$	80° C.	2.6	0.5	84
$Zn(BF_4)_2.7H_2O$	50° C.	1.3	0.0	81
$Zn(BF_4)_2.7H_2)$	80° C.	3.4	1.8	130
$CuCl_2.2H_2O$	50° C.	1.6	0.4	95
$CuCl_2.2H_2O$	80° C.	3.2	2.0	141
$Zn(NO_3)_2.6H_2O$	50° C.	1.7	0.3	81
$Zn(NO_3)_2.6H_2O$	80° C.	3.7	2.0	117
NH_4Cl	50° C.	1.9	1.1	147
NH_4Cl	80° C.	3.4	2.6	147
Untreated Control	-	-	-	75

Methyl Formcel/Formic Acid

The combination of methanol hemiformal (55% formaldehyde in methanol) and formic acid should offer a good vapor phase crosslinking system for pure cotton. Table 6 summarizes some of the results obtained on the cotton fabrics by vapor phase exposures to this system. Also, there are shown data obtained on the same fabrics by padding with various aqueous solutions of Methyl Formcel and 1% zinc nitrate catalyst, followed by frame drying 5 minutes at 250° F. and curing 5 minutes at 300° F., followed by a process wash and drying. Figures 1 and 2 graphically show the dramatic difference between the abrasion-crease resistance curve of the pad-dry-cure method versus that of vapor phase crosslinking at low temperatures. These differences are not superficial as are those given by lubricants and softeners. Here, no lubricants, softeners, nor any thermoplastic polymers were present in either set of fabrics. We believe that these improved abrasion values result from improved fiber toughness produced by crosslinking the cellulose in an uncollapsed state in the vapor phase (6-8% moisture was present in the fibers). Also a contributing factor may be the low temperatures of 50-80C., in which the crosslinking was accomplished. At the low level of crease resistance (MCRA) there appears to be a slight increase in flex abrasion over that of the control. This is real, as will be seen in later cases with chlorosilane-DMEU crosslinking. Note also that at equal MCRA performance level, the fabric tensile strength is also higher for the vapor phase treated samples.

METHYL FORMCEL

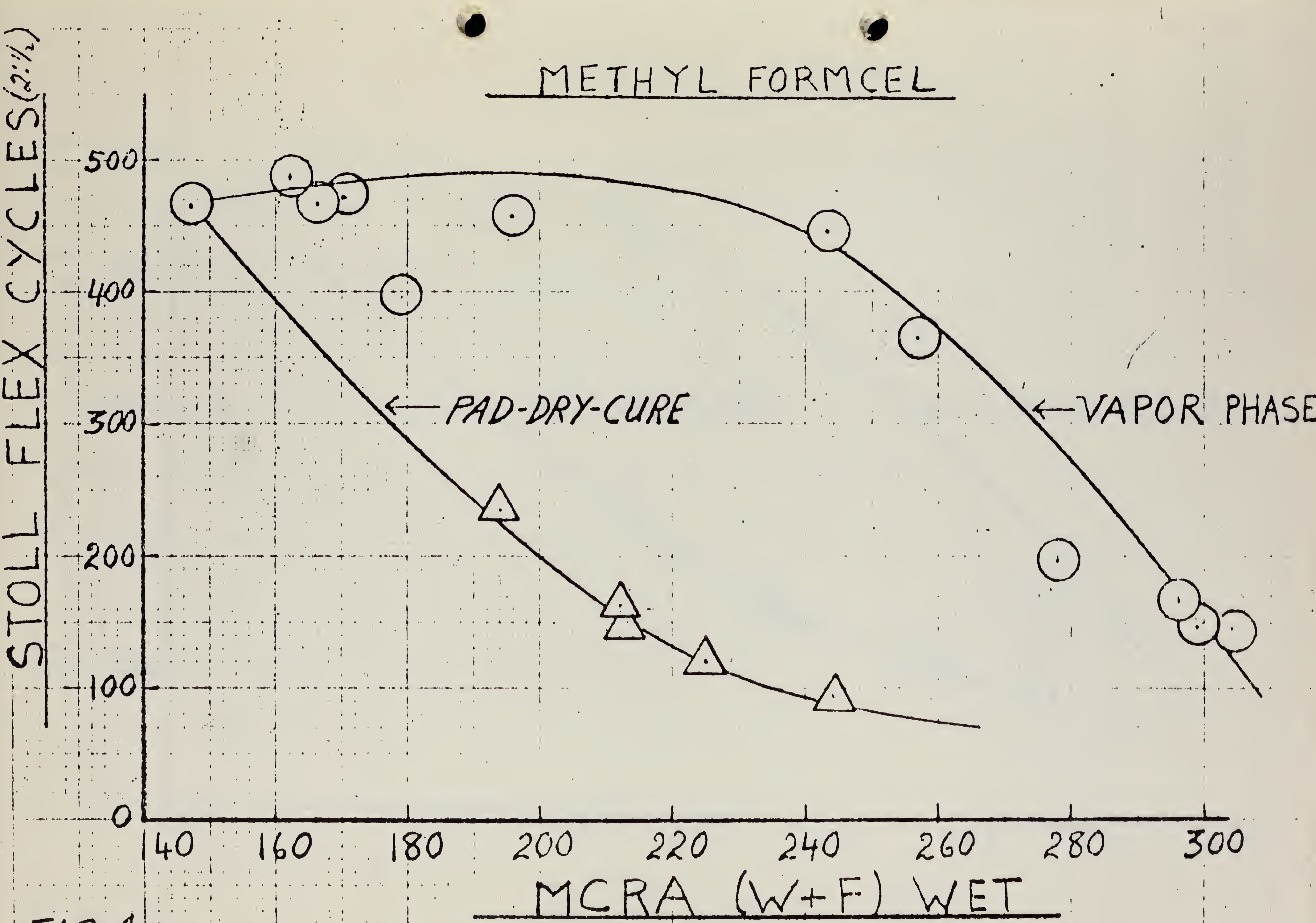


FIG. 1

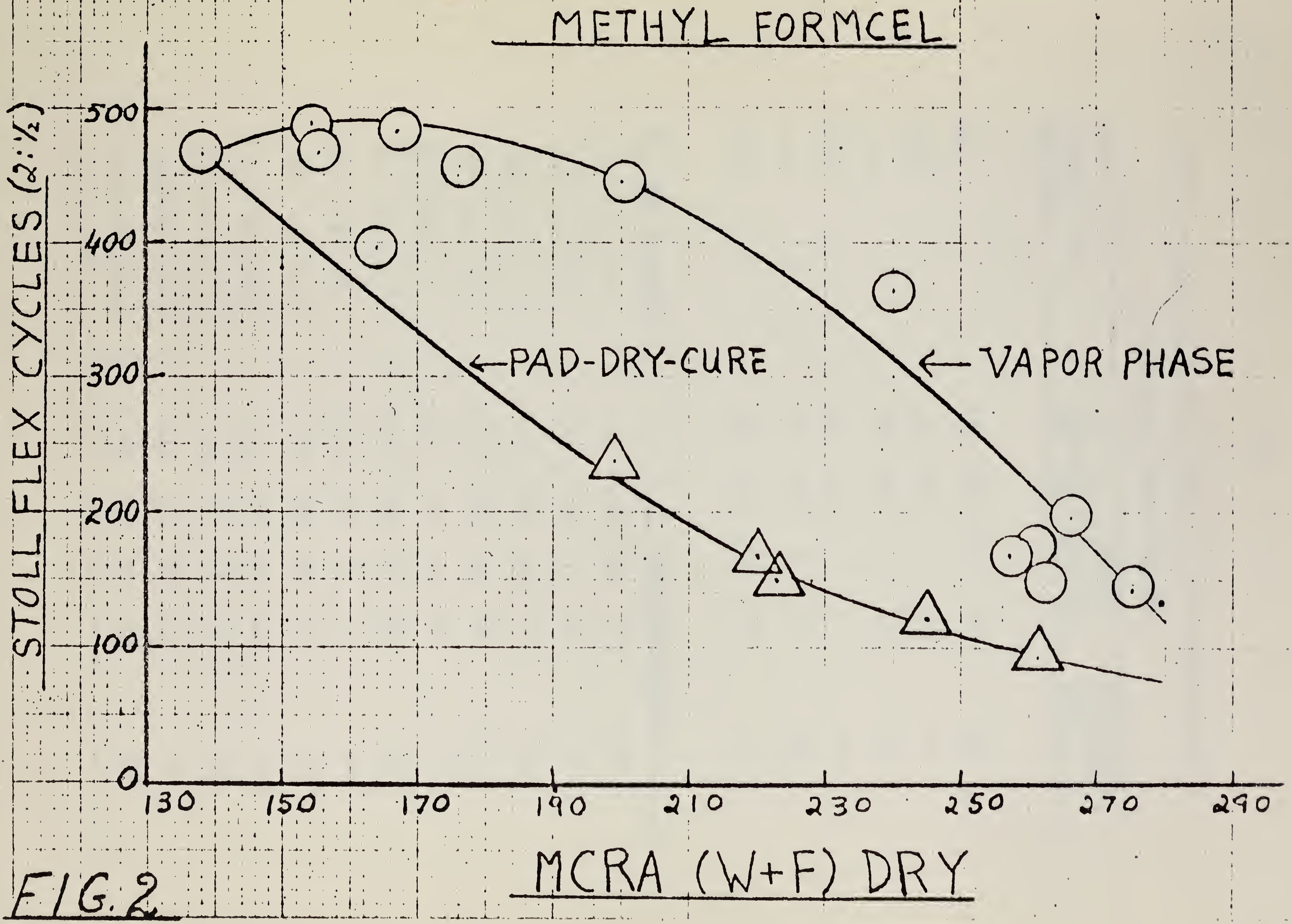

METHYL FORMCEL
STOLL FLEX CYCLES (2:½)
500
400
300
200
100
0
130
150
170
190
210
230
250
270
290
←PAD-DRY-CURE
← VAPOR PHASE
MCRA (W+F) DRY

FIG. 2

TABLE 6.--Vapor phase crosslinking of cotton versus pad, dry cure process (Methyl Formcel)

% CH_2O By Pad, Dry, Cure	MCRA (W+F) Dry	MCRA (W+F) Wet	Tensile Lbs./in. W	Tensile Lbs./in. F	Stoll Flex (2:1/2 Lbs.) Cycles - W
None	138	147	60	42	466
0.5%	199	194	25	18	233
1.0%	220	212	24	17	161
2.0%	223	213	26	17	159
4.0%	245	225	20	14	120
6.0%	261	244	20	14	93
Gms. MFC in Reactor			Vapor Reactions		
180/4 Hrs./50°C.	164	179	46	37	397
135/4 Hrs./50°C.	167	170	51	39	471
90/4 Hrs./50°C.	155	166	56	35	466
45/4 Hrs./50°C.	154	162	52	36	484
180/8 Hrs./50°C.	176	196	51	32	458
180/16 Hrs./50°C.	200	243	41	26	446
180/4 Hrs./80°C.	240	257	33	22	362
180/16 Hrs./80°C.	257	296	22	14	167
180/24 Hrs./80°C.	262	299	19	14	147
134/16 Hrs./80°C.	275	304	23	14	144
90/16 Hrs./80°C.	259	295	21	15	175
45/16 Hrs./80°C.	264	278	21	15	196

Tests using a 1% NH_4Cl catalyst were also studied for this system. The catalyst was padded and dried in the cotton samples which were then exposed to vapors of methyl formcel at 80°C. for various periods of time. By weight gain analysis, less than 1% formaldehyde was found in the extracted samples. The wet and dry crease resistance produced was, however, very substantial. See Table 7. As can be seen here, higher dry than wet crease resistance was given by this method of catalysis.

In Table 8 are shown other data obtained using formic acid as the vapor phase catalyst. In one case, the samples were exposed to the vapors of the catalyst and methyl formcel, scoured and dried. In the other case, the samples after exposure were post cured for 5 minuted at 300°F. before scouring. As can be seen, the vapor phase reaction alone produced crease resistance. In this case, however, the wet crease resistance was higher than that of the dry. This is in contrast to the NH_4Cl dried-in system used above and appears to be characteristic of vapor phase catalyzed crosslinking.

TABLE 7.--Wet and dry crease resistance produced by Methyl Formcel on 1% NH_4Cl Preimpregnated cotton

Exposure time at 80°C.	Warp crease resistance	
	Wet	Dry
15 minutes	60	73
30 minutes	60	75
60 minutes	84	100
120 minutes	134	123
240 minutes	144	138
480 minutes	153	147

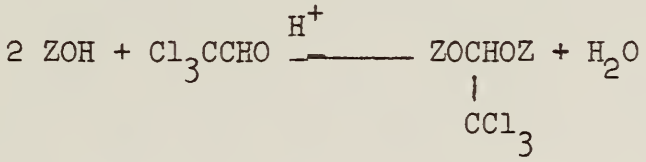
Table 8.--Vapor phase catalyzed reaction of Methyl Formcel

Reaction Temp. 24 hrs.	Warp crease resistance			
	Vapor only		Post cured	
	Wet	Dry	Wet	Dry
30°C.	82	74	94	86
40°C.	94	79	90	87
60°C.	123	98	112	113
80°C.	149	141	143	149

Crosslinking With Other Aldehydes

With the methanol hemiformal (CH_3OCH_2OH Methyl Formcel) good fiber reaction is obtained both on catalyst preimpregnated cotton and in vapor phase catalysis with formic acid and HCl. High wet crease resistance is obtained with the vapor phase catalysis. Since other aldehydes have received little or no attention as finishing agents for cotton because of problems of volatility in normal wet pad applications, and since some of these might offer other properties not given by formaldehyde, some explorations were made with vapor phase reactions.

In all of these aldehyde reactions it was assumed that cellulose (ZOH) crosslinking would result as shown below for chloral:



$$2\ \mathrm{ZOH} + \mathrm{Cl_3CCHO} \xrightarrow{H^+} \underset{\substack{|\\ \mathrm{CCl_3}}}{\mathrm{ZOCHOZ}} + \mathrm{H_2O}$$

This specific case is a good example of a reaction that cannot be carried out in normal wet finishing operations because of the toxicity of chloral and its hydrate, chloral hydrate. Such a reaction, if successful, might offer the dual property of creaseproofing and flame resistance, due to the high amount of chlorine present in the compound.

In a first trial cotton fabrices were preimpregnated with various acidic catalysts and dried. These were placed in a vapor reactor and no vacuum applied. The chloral was allowed to reflux at 98-105°C. The cloth samples were suspended in the vapors of chloral. After one hour exposure, the samples were removed, scoured with 0.25% Na_2CO_3 and 0.1% Tergitol NPX for 15 minutes at 60°C., rinsed and dried. As shown in Table 9, no indication of fiber reaction is evident from weight gain analysis. In fact, a weight loss had occurred with all catalysts. Also, the fabrics were very weak, even without catalyst.

In a second attempt, various aldehydes, hydrates or acetals were used in a closed system which contained the vapors of the reagents at the specified temperature. Here cotton fabrics were preimpregnated with 1% NH_4Cl which is a universal catalyst for aldehyde reactions with cellulose. The exposure was for 24 hours, after which the samples were weighed, scoured as before stated and reweighed. The results are shown in Table 10. These are compared with similar runs previously made with Methyl Formcel in a similar closed system.

The first weighing showed that the cloth had absorbed the various aldehyde vapors during the exposure. Only in the case of the hemiformal is there positive weight gain and high crease resistance found after acouring. Slight indication of reaction is shown by paraldehyde at 50°C., i.e., crease resistance of 85 and 101 MCRA.

TABLE 9.--Vapor phase reaction of chloral on catalyst impregnated cotton:

1 hour at 98-105°C.

Catalyst on Fabric	Bone dry sample weight Initial	 Reacted/extracted
None	1.826	1.765
1% $MgCl_2$-$6H_2O$	1.864	1.809
0.4% $Zn(BF_4)_2$	1.848	1.821
1% $CuCl_2 \cdot 2H_2O$	1.881	1.821
1% $Zn(NO_3)_2 \cdot 6H_2O$	1.848	1.823
1% NH_4Cl	1.953	18 72

TABLE 10.--Vapor phase reaction of various aldehydes on 1% NH_4Cl preimpregnated cotton

Aldehyde used	Temp. °C. 24 Hrs.	% Weight gain		Warp crease resistance	
		Initial	Extracted	Dry	Wet
CH_3OCH_2OH	30	1.88	1.09	134	--
$Cl_3CH(OH)_2$	30	6.07	-0.14	75	79
Cl_3CHO	30	6.40	-0.54	69	81
C_6H_5CHO	30	6.00	-0.14	71	77
$(CH_3CHO)_3$	30	6.03	-0.05	57	74
CH_3OCH_2OH	50	1.90	1.10	147	--
$Cl_3CH(OH)_2$	50	4.72	-1.12	78	98
Cl_3CHO	50	4.61	-5.12	weak	weak
C_6H_5CHO	50	5.16	-0.16	67	76
$(CH_3CHO)_3$	50	4.74	-2.10	85	101

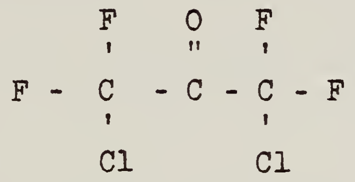
In a third trial, a vapor phase catzlysis was attempted in a closed system. Here 10 gms. samples of cotton were placed in a one liter jar which contained two 50 milliliter beakers. In one were placed 25 gms. of aldehyde. In the other were placed 30 gms. of formic acid. After sealing the jars, they were placed in an oven for 24 hours at 50°C. The results are shown in Table 11. In this case, high weight gain was found due to absorbed aldehyde vapors. After scouring, positive weight gain was found in all cases. Both the chloral and chloral hydrate samples were very weak and broke during the crease test. These showed the highest weight gain. The paraldehyde produced some weight gain and crease resistance. The least effect was found with benzaldehyde and tetraethoxypropane. From these results it appears possible to obtain vapor phase reactions of cotton with various aldehydes.

TABLE 11.--Vapor phase reaction of various aldehydes on cotton; vapor phase catalysis with formic acid

Aldehyde used	Temp. °C. 24 hrs.	% Weight gain Init.	Extr.	Warp crease resistance Dry	Wet
CH_3OCH_2OH	60	3.69	1.45	98	123
$Cl_3CH(OH)_2$	50	13.50	2.57	--	--
Cl_3CHO	50	42.50	3.90	--	--
C_6H_5CHO	50	6.44	0.04	64	71
$(CH_3CHO)_3$	50	9.87	1.55	109	103
$(C_2H_5O)_2CHCH_2CH(OC_2H_5)_2$	50	5.86	0.04	73	82

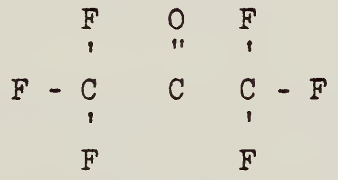
Perfluoro Ketone Crosslinking

Two fluorinated ketones have recently become available. The first of these is a liquid boiling at 45.2°C.:



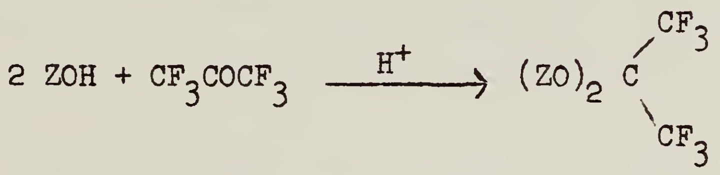
$$\mathrm{F-\overset{F}{\underset{Cl}{C}}-\overset{O}{\overset{\|}{C}}-\overset{F}{\underset{Cl}{C}}-F}$$

The second is a gas boiling at -27.4°C.:



$$\mathrm{F-\overset{F}{\underset{F}{C}}\;\overset{O}{\overset{\|}{C}}\;\overset{F}{\underset{F}{C}}-F}$$

Both of these ketones are listed as reactive materials which can form ketals with alcohols. We assumed that similar reaction is possible with cellulose (ZOH):



$$2\ \mathrm{ZOH} + \mathrm{CF_3COCF_3} \xrightarrow{H^+} \mathrm{(ZO)_2\,C(CF_3)_2}$$

If such a reaction could be accomplished in a vapor phase, it might produce crosslinking of cotton and also provide a high density of perfluoro groups which could yield water, oil and soil repellency.

A first attempt to achieve such an effect was involved with various means of catalyzing the reaction. Both vapor phase acid catalysis and cloth preimpregnation were attempted. A refluxing system was used. After exposure, the cotton samples were weighed, extracted with dioxane, water and 1% $NaHCO_3$, dried and reweighed. The results are shown in Table 12. No reaction between the dichloro tetrafluoro acetone and cotton was achieved under these conditions.

Chloromethyl Ether

As previously mentioned, one of the practical problems to be resolved for commercial use of a vapor phase permanent-press process is that of reaction times. One attempt to do this involved the use of chloromethyl ether -CH_3OCH_2Cl instead of its Methyl Formcel analog -CH_3OCH_2OH. The chloromethyl ether could act both as a crosslinking agent:

$$2ZOH + CH_3OCH_2Cl \longrightarrow ZOCH_2OZ + HCl + CH_3OH$$

and its own acid catalyst, since it releases HCl on contact with water or cellulose. This might give fast reaction times at low temperatures.

In a first attempt, untreated cotton and cotton pretreated with 5% urea were exposed to vapors of chloromethyl ether for short-time periods. Short-time periods. Some crosslinking occurred as noted by the rise in wrinkle resistance, Table 13 especially in the untreated cotton. This approach has some merit and should be further studied.

TABLE 12.--Attempted etherification of cotton with vapors of dichloro tetrafluoro acetone

Catalyst on cloth	Pot temp. °C.	Vapor temp. °C.	Time of heat	% Weight gain Init.	Extr.
None	41-47	39-47	1 hr.	0	0
0.5% $CaCl_2$	36-46	35-45	1 hr.	0.80	0
0.5% $Zn(NO_3)_2 \cdot 6H_2O$	38-46	37-46	1 hr.	0.64	0
0.2% $Zn(BF_4)_2$	37-47	37-50	1 hr.	0.67	0
1% Oxalic acid	40-41	40-47	1 hr.	0.84	0.52
1% Oxalic acid	39-49	38-49	5 hrs.	0.72	0
2% NH_4Cl	37-46	38-50	1 hr.	2.42	0
2% H_3PO_4	35-46	36-48	1 hr.	2.06	0
90 DTA) 10 TFA)[1]	33-46	33-47	1 hr.	0.50	0
90 DTA) 10 HCl)[1]	60-83	54-79	1 hr.	0	0

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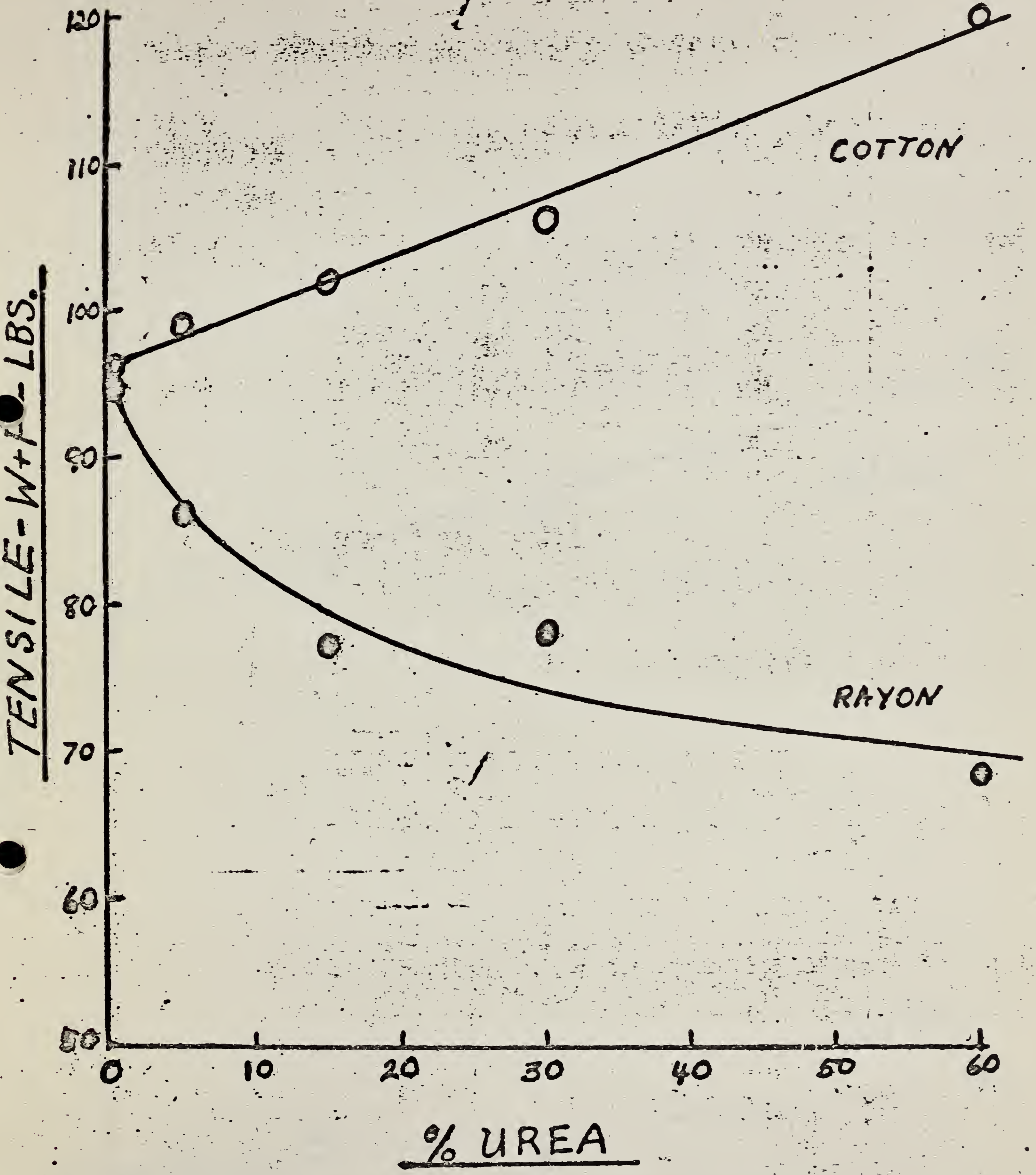
[1] No catalyst on cloth; vapors of DTA/catalyst only.

TABLE 13.--Vapor phase crosslinking with chloromethyl ether

Exposure time at 50°C.	MCRA (W + F) Dry	Wet
Untreated	147	113
1 min.	167	158
5 mins.	199	173
10 mins.	211	175
15 mins.	205	169
5% Urea	147	113
1 min.	180	162
5 mins.	177	173
10 mins.	182	181
15 mins.	172	172

5-4E



TENSILE-W+F-LBS.
120
110
100
90
80
70
60
50
0
10
20
30
40
50
60
% UREA
COTTON
RAYON

Figure 3

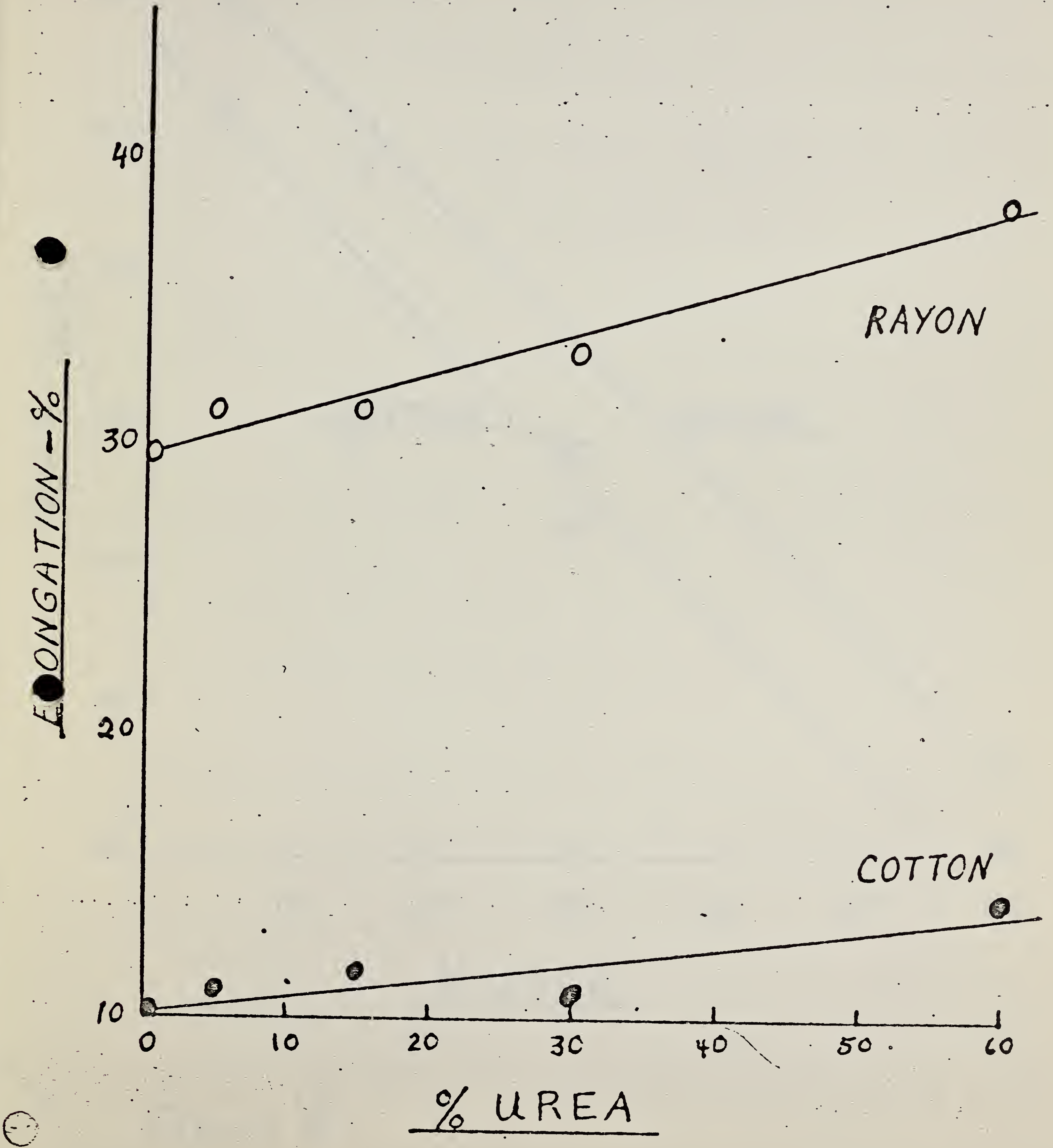
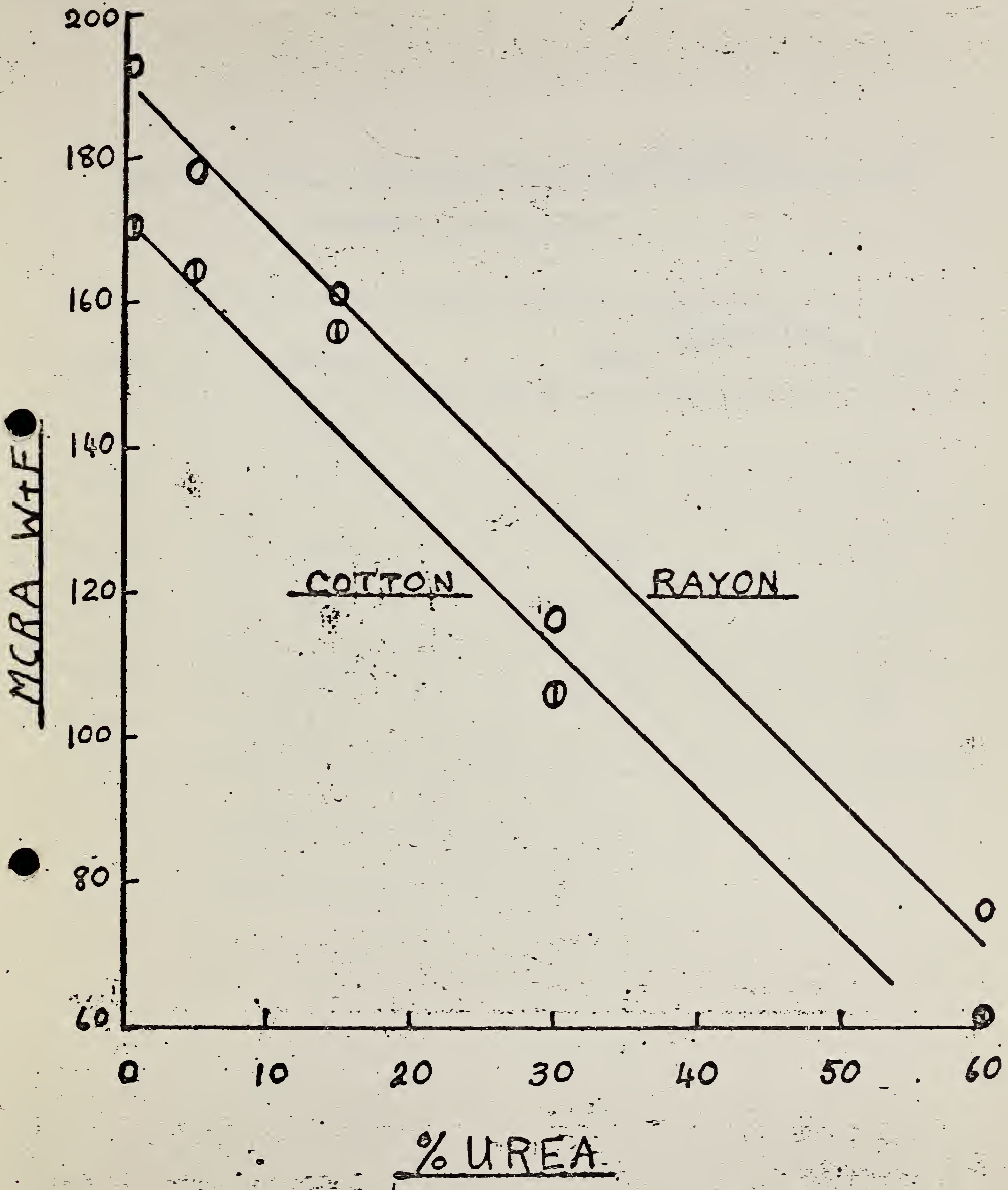


Figure #4



200
180
160
140
120
100
80
60
MCRA WtF
COTTON
RAYON
0
10
20
30
40
50
60
% UREA

Figure # 5

TABLE 14.--Relative imbibitions by untreated and treated (crosslinked) celluloses of water and urea solutions

Fabric	Treatment	% Imbibition[a]	
		Water	50% Urea[b]
Linen	None	31	49
Linen	X-L	26	35
Cotton	None	48	66
Cotton	X-L	42	58
Rayon	None	66	91
Rayon	X-L	47	65

a/ By dynamic absorption tester.

b/ Specific gravity of 1.150 at 15°C.

TABLE 15.--Relative imbibition by cellulose of water and DMEU solutions

% DMEU In solution	% Imbibition a/ Linen	 Cotton	 Rayon
Water only	59	74	75
5%	71	75	92
10%	74	76	92
20%	74	79	98
30%	79	84	99
50%	76	86	101

a/ By padding after 1 hour soak.

It would be desirable if this effect could be "frozen-in" the cotton fibers by fixing the urea through a vapor phase formaldehyde reaction. Aqueous impregnations are not possible here, since the dried-in urea would leach out. Also, in such an approach with urea, or with other nitrogen compounds useful for crosslinking, the possibility is available to form resins or fiber reactants within the swollen fiber itself. For example, one could impregnate cotton with swelling concentrations of:

urea
dihydrazides
ethylene urea
ethyl carbamate
propylene urea
Uron
triazone
4,5-dihydroxyethylene urea
formamide
succinamide

then dry the fabrics. Subsequently, through a vapor phase reaction with formaldehyde, the bis hydroxymethyl derivatives could be formed *in situ* within the fibers and the reaction with the fibers be carried out simultaneously.

The formation of resins and/or the crosslinking reactions with cotton through vapor phase techniques was explored with urea as a model. Cotton was pad pretreated with increasing concentrations of urea followed by drying five minutes at 250°F. Then the individual specimens were placed in the sealed jars and exposed to vapors of formaldehyde from methyl formcel. Solutions of HCl in a separate container were also put in the reaction jars to serve as the vapor phase catalysts. After one day exposure at 21°C., the specimens were reweighed. Then they were extracted, dried, reconditioned and again weighed.

The results of these explorations are shown first in Table 16. Here 6-7 grams of urea preimpregnated cotton were exposed to the vapors of 18 grams of 55% methyl formcel and of 5.0 mls. of conc. HCl in 25 mls. of water. While in all cases there is sufficient formaldehyde supplied to form monomethylol to polymethylol ureas in the fibers, apparently this is not all available in the vapor phase. About 1% total fixed resins were obtained in all samples regardless of the urea content of the cotton.

TABLE 16.--Vapor phase reactions with methyl Formcel on urea impregnated cotton to produce internal resins and crosslinking at 21°C. (HCl vapor catalyst[a])

% Urea applied	% Urea deposited	% Weight gain - urea Formcel Initial	Fixed	% Retention[b]
5% A	3.5	4.6	0.9	26
5% B	3.3	4.3	0.9	27
10% A	8.4	9.4	0.4	5
10% B	8.2	9.2	1.1	13
15% A	12.9	14.2	0.5	4
15% B	13.0	13.9	0.9	7
20% A	18.0	19.3	0.5	3
20% B	17.8	19.1	0.7	4
25% A	23.6	24.9	-0.2	0
25% B	23.3	24.6	0.2	1

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[a] 5.0 Mls. conc. HCl in 25 ml. of H_2O.

[b] Based on urea deposited.

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

[illegible]

[illegible]

In a second experiment the conditions were repeated, but the amount of HCl increased to 7.5 mls. The results are shown in Table 17. Note now the greater development of fixed resins. Also, note the greater retention or percent fixation of the urea applied. High yields were found at the low urea concentration levels. In a third experiment, the HCl content was further increased to 15 mls. (Table 18.) Even higher yields were obtained. Within each of three experiments, the amount of fixed resins seems to be independent of the amount of urea present in the fibers. This certainly should not be so and indicates that insufficient formaldehyde must be present in the vapor phase.

Before learning that these conditions of treatment were not supplying enough formaldehyde inthe vapors at 21°C. and 24 hours exposure, a separate experiment had been started with stronger swelling concentrations of urea. In this case, one half of the sample was exposed only and scoured while the other half was heated at 300°F. for 10 minutes before scouring. The results are shown in Tables 19 and 20. The heated samples showed higher weight gain. Again the retnetion value is seen to decrease with increasing urea content in the fibers confirming the insufficiency of formaldehyde vapors in the container.

TABLE 17.--Vapor phase reactions with Methyl Formcel on urea impregnated cotton to produce internal resins and crosslinking at 21°C. (HCl vapor catalysis)[a]

% Urea pplied	% Urea deposited	% Weight gain - urea + Formcel Initial	Fixed	% Retention[b]
5% A	3.7	4.6	2.7	73
5% B	3.4	4.5	2.7	79
10% A	7.9	8.6	2.8	35
10% B	7.7	9.5	3.6	47
15% A	12.0	15.5	3.4	28
15% B	12.4	13.2	3.2	26
20% A	17.4	22.6	1.8	10
20% B	16.5	23.6	2.6	16
5% A	22.6	18.1	1.6	7
5% B	22.0	18.9	2.6	12

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a/ 7.5 Ml. of conc. HCl in 22.5 ml. of H_2O.

b/ Based on urea deposited.

TABLE 18.--Vapor phase reactions with methyl formcel on urea impregnated cotton to produce internal resins and crosslinking at 21°C. (HCl vapor catalyst)[a]

% Urea applied	% Urea deposited	% Weight gain - urea + Formcel Initial	Fixed	% Retention[b]
5% A	3.7	4.7	3.1	84
5% B	3.4	8.4	2.5	74
10% A	7.9	9.5	4.1	52
10% B	7.7	9.3	3.5	45
15% A	12.0	16.3	3.5	29
15% B	12.4	13.9	4.8	39
20% A	17.4	18.7	2.9	17
20% B	16.5	18.5	5.2	31
25% A	22.6	23.9	2.2	10
25% B	22.0	24.3	3.0	14

[a] 15 Ml. of conc. HCl in 15 ml. of H_2O.

[b] Based on urea deposited.

TABLE 19.--Vapor phase reactions with Methyl Formcel on urea impregnated cotton to produce internal resins and crosslinking (HCl vapors catalyst)[a]

% Urea applied	Vapor catalyst[a]	% Weight gain urea + Formcel Initial	 Fixed
20	7.5 ml.HCl	22.0	1.6
40	7.5 ml.HCl	50.0	1.4
50	7.5 ml.HCl	57.0	1.0
20	15.0 ml.HCl	23.0	3.9
40	15.0 ml.HCl	49.0	1.6
50	15.0 ml.HCl	58.0	1.4

[a] Mls. of conc. HCl in total of 30 ml. H_2O solution; no cure after exposure to vapors.

TABLE 20.--Vapor phase reactions with Methyl Formcel on urea impregnated cotton to produce internal resins and crosslinking (HCl vapors catalysis)[a]

% Urea applied	Vapor catalyst[a]	% Weight gain urea + Formcel Initial	Fixed
20	7.5 mls HCl	22.0	2.2
40	7.5 mls HCl	50.0	1.3
50	7.5 mls HCl	55.0	1.2
20	15.0 mls HCl	23.0	4.4
40	15.0 mls HCl	47.0	2.2
50	15.0 mls HCl	58.0	2.2

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[a] Mls. of conc. HCl in total of 30 ml. H_2O solution; with cure of 10 min./300°F. after exposure to vapors.

Samples of cotton fabric weighing about 6.0 grams were exposed in sealed 1000 cc. polyethylene jars to the vapors of 18 grames of 55% Methyl Formcel and 30 grams of formic acid catalyst in one case or 5 ml. of concentrated HCl in 25 ml. of water in another case. The jars were placed in an air circulating oven for 24 hours at the stated temperature. Then they were analyzed for weight gain, urea content, formaldehyde absorbed and fixed resin. Another set was cured for 5 minutes at 300°F. after removal from the jar and before extraction. Wet and dry warp crease resistance measurements and filling tensiles were made.

In the system chosen there is present in each chamber 10 grams of formaldehyde which is potentially available from the methyl formcel. This formaldehyde is in excess of the amount needed to form dimethylol urea in the fabric, even at the 50% urea concentration used for some samples:

For dimethylol urea, the F:U ratio is 2:1
For 6 grams of fabric x 50% urea - 3 grams of urea
3 grams urea - 0.05 mole
10 grams CH_2O - 0.33 mole

Therefore, the maximum possible ratio for the 50% urea content case is F:U of 6.6:1. Consequently, for all the urea concentrations studied, there is potentially available more than enough formaldehyde to form the first reactant, dimethylol urea in all cases.

In the above vapor phase reaction we have the following chemical system:

<u>In the solid phase</u>: Cellulose - ZOH
Urea - NH_2CONH_2

<u>In the vapor phase</u>: Formaldehyde - CH_2O
Methanol - CH_3OH
Catalyst - HCOOH or HCl

If the urea in the cellulose is accessible to the formaldehyde and catalyst, then it is hoped to accomplish the following reactions in the urea swollen regions of the cotton:

Formation of dimethylol urea-DMU:

$$NH_2CONH_2 + 2\ CH_2O \longrightarrow HOCH_2NHCONHCH_2OH$$

<u>Reaction of DMU with cellulose-ZOH</u>:

$$2\ ZOH + HOCH_2NHCONHCH_2OH \longrightarrow ZOCH_2NHCONHCH_2OZ + 2\ H_2O$$

A number of other reactions, however, are also possible:

<u>Cellulose formalization</u>:

$$2\ ZOH + CH_2O \longrightarrow ZOCH_2OZ + H_2O$$

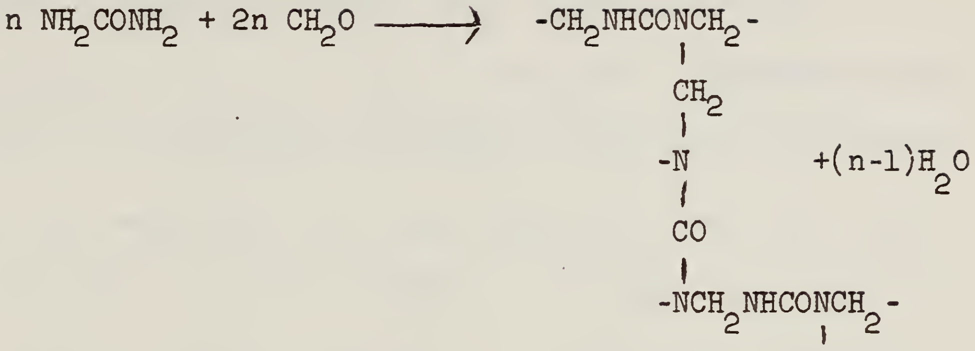
This would yield only low weight gain, based on previous observations.

<u>Alkoxymethylation of cellulose</u>:

$$ZOH + CH_2O + CH_3OH \longrightarrow ZOCH_2OCH_3 + H_2O$$

Such a reaction would not produce crease resistance.

Resin formation:



$$n\ NH_2CONH_2 + 2n\ CH_2O \longrightarrow \begin{array}{c} -CH_2NHCONCH_2- \\ | \\ CH_2 \\ | \\ -N \\ | \\ CO \\ | \\ -NCH_2NHCONCH_2- \\ | \end{array} \quad +(n-1)H_2O$$

Such a reaction would lead to high weight gain and crease resistance if some of the methylol groups reacted with the cellulose. As has been the case with previous treatments of cotton with preformed dimethylol urea in pad-dry-cure systems, it is not easy to resolve how much of each of the above side reactions would take place in a vapor treatment.

The gravimetric analyses of the results obtained in the formic acid/Methyl Formcel vapor reaction on urea preimpregnated cotton are shown in Table 21. Thesedemonstrate the amount of formaldehyde absorbed (or reacted) as a function of reaction temperature and urea content of the cotton fabric. From these data, the formaldehyde to urea ratio was calculated for the fabrics before extraction. The F/U ratio increased with reaction temperature at all urea concentrations used. The overall F/U ratio decreased, however, as the urea content of the fabrics increased. Since in each reaction vessel there is potentially available enough formaldehyde to form the desired dimethylol urea (F/U of 2:1) it must be concluded that either not enough formaldehyde is available in the vapor phase or that not all of the urea in the fibers is available to the formaldehyde vapors as the urea content increases.

TABLE 21.--Resin formation through vapor phase reaction of $CH_3OCH_2OH/HCOOH$ with urea preimpregnated cotton[1]

Urea sol'n. applied	Reaction temp.	% Urea deposited	% HCHO absorbed	Mole % urea	Mole % HCHO	Ratio F/U
5%	30°C.	3.70	6.58	0.061	0.219	3.6
5%	40°C.	3.04	6.74	0.051	0.225	4.4
5%	60°C.	3.76	7.89	0.063	0.263	4.2
5%	80°C.	3.57	10.03	0.060	0.334	5.6
10%	30°C.	8.99	9.92	0.150	0.337	2.2
10%	40°C.	7.42	9.17	0.124	0.306	2.5
10%	60°C.	9.23	10.92	0.154	0.364	2.4
10%	80°C.	8.70	14.04	0.145	0.468	3.2
20%	30°C.	19.38	10.50	0.323	0.350	1.1
20%	40°C.	16.50	10.90	0.275	0.363	1.3
20%	60°C.	19.20	14.15	0.320	0.472	1.5
20%	80°C.	19.50	19.74	0.325	0.658	2.0
40%	30°C.	41.33	8.12	0.689	0.276	0.4
40%	40°C.	35.25	12.36	0.588	0.412	0.7
40%	60°C.	40.35	21.05	0.673	0.702	1.0
40%	80°C.	39.55	30.50	0.659	1.017	1.8

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[1] The data represents the average of two tests in all cases.

In Table 22 are shown the combined weight gains (urea + formaldehyde absorbed) and the "fixed resins" or final weight gain found after extraction of water soluble unreacted materials from the fibers. Two sets of fixed resins are shown. The first are those produced by the vapor phase exposure alone. The second are those found after a postcure of the vapor absorbed formaldehyde. Examination of the two sets of values over the whole range of urea concentrations shows that the reaction with formaldehyde is essentially complete during the vapor exposure. Postcuring the fabrics for 5 minutes at 300°F. causes only a slight increase in fixed resin yield. Further examination also shows that while the vapor reaction temperature has definite influence on the weight of formaldehyde absorbed it has little effect on the final weight gain or "fixed resin" formation except at the 40% urea concentration. With the latter, increased yield is found with a rise in temperature.

In Table 23 are shown the wet and dry crease resistance produced by the vapor treatments on the urea preimpregnated fabrics. Here very high wet crease resistance and high wet to dry crease resistance ratios were produced, especially at the 10% urea level. Higher concentrations of urea begin to cause fiber cementing and stiffness. Some data on cotton treated with preformed methylol urea by the pad-dry-cure procedure are shown in Table 24 for comparison. In no case were the results comparable to those shown in Table 23 for either wet crease resistance or for total dry and wet crease resistance levels.

TABLE 22.--Resin formation through vapor phase reaction of CH_3OCH_2OH/HCOOH with urea preimpregnated cotton

Urea sol'n. applied	Reaction temp.	Initial weight gain-%	Fixed Resins	
			Vapor only	Post cured
5%	30°C.	10.28	6.9	7.4
5%	40°C.	9.78	5.6	6.5
5%	60°C.	11.65	7.1	7.1
5%	80°C.	13.60	5.1	6.7
10%	30°C.	18.91	14.5	15.1
10%	40°C.	16.59	11.8	13.3
10%	60°C.	20.15	14.5	14.2
10%	80°C.	22.74	8.0	11.4
20%	30°C.	29.88	24.3	26.2
20%	40°C.	27.40	22.3	22.4
20%	60°C.	33.35	23.5	24.6
20%	80°C.	39.24	20.3	21.0
40%	30°C.	49.45	22.1	26.1
40%	40°C.	47.61	38.3	38.5
40%	60°C.	61.40	50.1	55.8
40%	80°C.	70.05	43.1	50.4

TABLE 23.--Resin formation through vapor phase reaction of $CH_3OCH_2OH/HCOOH$ with urea preimpregnated cotton and warp crease resistance (MCRA)

Urea sol'n. applied	Reaction temp.	Vapor only MCRA Wet	Vapor only MCRA Dry	Vapor only Tensile strength [1]	Postcured MCRA Wet	Postcured MCRA Dry	Postcured Tensile strength [1]
5%	30°C.	136	94	26	129	122	27
5%	40°C.	132	117	26	137	136	24
5%	60°C.	138	137	20	143	138	18
5%	80°C.	138	114	17	144	131	--
10%	30°C.	139	123	27	140	132	26
10%	40°C.	129	129	26	148	145	27
10%	60°C.	154	143	23	143	141	20
10%	80°C.	140	111	16	143	115	--
20%	30°C.	128	87	30	110	90	29
20%	40°C.	127	107	28	134	113	23
20%	60°C.	142	97	28	143	123	27
20%	80°C.	140	111	20	142	115	18
40%	30°C.	87	61	44	93	48	40
40%	40°C.	98	61	23	120	68	32
40%	60°C.	133	80	27	122	77	31
40%	80°C.	125	83	21	134	88	25

1/ Filling tensile-lbs./in.

TABLE 24.--Conventional pad-dry-cure treatment of cotton with a methylol urea condensate[1] (Compare with Table 3)

% Solids applied	Warp crease recovery angle (MCRA) Wet	Dry	Fill tensile lbs./in.
4.3	103	89	32
8.6	108	107	29
12.9	119	103	29
17.2	118	128	27
25.8	122	124	24
34.4	111	133	26
43.0	112	123	30
51.6	112	103	30

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[1] F/U ratio of 1.33/1; 1.5% catalyst AC dry 5'/250°F.; Cure 5'/300°F.

The results in Table 24 clearly demonstrate that a vapor phase reaction of formaldehyde with urea impregnated cotton can be effected by the use of a volatile acid catalyst. Since the cotton fiber is not collapsed by any dry-cure step in this process and since it has been preswollen with urea, it could be concluded that resin formation or fiber crosslinking is occurring in different regions of the fibers from those normally available in the pad-dry-cure application of preformed methylol urea condensates. This is substantiated in part by the very high wet crease resistance produced in the vapor treatment.

In Tables 25, 26, and 27 are shown data for comparable vapor phase treatments using HCl as the volatile catalyst. The results differ from those found with formic acid in the following manner:

a. The formaldehyde absorbed is less, resulting in lower formaldehyde to urea ratios of all concentrations.

b. The fixed resins yields with or without cure are less than with formic acid.

c. In this case, the fixed resin yields are higher dependent on reaction temperature at all concentrations of urea.

d. Crease resistance is also highly dependent on reaction temperature.

e. The 80°C. samples are all much too weak for testing. Again, high wet and dry crease resistances are found with some of the samples. The formic acid catalysis, however, appears to be preferred since it is less temperature dependent, at least for the case of urea reactions.

TABLE 25.--Resin formation through vapor phase reaction of CH_3OCH_2OH/HCl with urea preimpregnated cotton

Urea sol'n. applied	Reaction temp.	% Urea deposited	% HCHO absorbed	Mole % urea	Mole % HCHO	Ratio F/U
5%	30°C.	3.98	2.92	0.066	0.097	1.5
5%	40°C.	3.98	4.31	0.066	0.144	2.2
5%	60°C.	4.19	5.11	0.070	0.170	2.4
5%	80°C.	--	--	--	--	--
10%	30°C.	8.65	2.10	0.144	0.070	0.5
10%	40°C.	8.16	5.49	0.136	0.183	1.3
10%	60°C.	9.73	7.22	0.162	0.241	1.5
10%	80°C.	--	--	--	--	--
20%	30°C.	18.85	2.94	0.316	0.098	0.3
20%	40°C.	18.60	4.90	0.311	0.163	0.5
20%	60°C.	20.72	10.88	0.346	0.363	1.0
20%	80°C.	--	--	--	--	--
[illegible]	[illegible]°C.	--	--	--	--	--
40%	30°C.	38.05	3.05	0.637	0.100	0.2
40%	40°C.	37.95	5.15	0.635	0.172	0.3
40%	60°C.	44.25	17.05	0.740	0.569	0.8
40%	80°C.	--	--	--	--	--

TABLE 26.--Resin formation through vapor phase reaction of CH_3OCH_2OH/HCl with urea preimpregnated cotton

Urea sol'n. applied	Reaction temp.	Initial weight gain-%	Fixed Resin	
			Vapor only	Post-cured
5%	30°C.	6.90	3.1	4.4
5%	40°C.	7.29	5.5	5.3
5%	60°C.	9.30	7.9	6.1
5%	80°C.	--	--	--
10%	30°C.	11.25	4.6	5.5
10%	40°C.	13.65	9.0	10.6
10%	60°C.	16.95	10.2	14.0
10%	80°C.	--	--	--
20%	30°C.	21.79	3.2	4.8
20%	40°C.	23.50	12.8	15.9
20%	60°C.	31.60	29.5	29.9
20%	80°C.	--	--	--
40%	30°C.	41.10	1.2	0.9
40%	40°C.	43.10	4.4	8.9
40%	60°C.	61.30	42.5	51.2
40%	80°C.	--	--	--

TABLE 27.--Resin formation through vapor phase reaction of CH_3OCH_2OH/HCl with urea preimpregnated cotton and warp crease resistance (MCRA) wet and dry crease resistance

Urea sol'n. applied	Reaction temp.	Vapor only MCRA Wet	Vapor only MCRA Dry	Postcured MCRA Wet	Postcured MCRA Dry
5%	30°C.	103	118	100	103
5%	40°C.	125	124	120	119
5%	60°C.	153	143	151	143
5%	80°C.	--	--	--	--
10%	30°C.	116	117	103	90
10%	40°C.	117	101	128	117
10%	60°C.	156	151	147	158
10%	80°C.	--	--	--	--
20%	30°C.	69	73	91	91
20%	40°C.	92	90	109	102
20%	60°C.	159	133	142	123
20%	80°C.	--	--	--	--
40%	30°C.	67	83	80	66
40%	40°C.	75	67	88	86
40%	60°C.	99	75	97	71
40%	80°C.	--	--	--	--

TABLE 28.--Materials balance in the vapor phase reaction of Methyl Formcel

on urea impregnated cotton

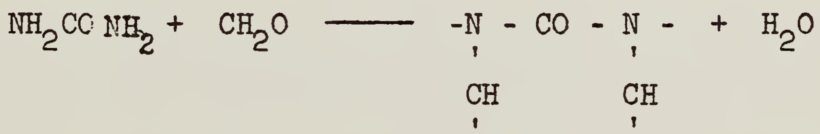
% Weight gain (A)	% Urea (C)	% $\left(\frac{-CH_2-}{A-C}\right)$	Mols % $\left(\frac{C}{60}\right)$ of urea	Mols % of CH_2O $\frac{30(A-C)}{12} \times \frac{1}{3}$	CH_2O/Urea ratio	CH_2O Combined with ZOH mols %
1B 7.41	5.63	1.78	0.094	0.148	1.57	0.000
2B 6.51	4.38	2.13	0.073	0.177	2.42	0.031
3B 7.07	3.99	3.08	0.066	0.256	3.88	0.124
4B 6.66	0.63	6.03	0.011	0.502	4.56	0.480
1C 15.1	6.18	8.92	0.103	0.741	7.20	0.535
2C 13.3	10.02	3.28	0.167	0.275	1,62	0.000
3C 14.2	9.48	4.72	0.158	0.393	2.53	0.077
4C 11.4	9.68	1.72	0.161	0.143	0.900	0.000
1D 26.2	15.94	10.26	0.299	0.855	2.87	0.257
2D 22.4	14.53	7.86	0.242	0.638	2.67	0.154
3D 24.6	7.14	17.46	0.119	1.450	12.10	1.212
4D 21.0	10.72	10.81	0.170	0.900	5.30	0.560
1E 26.1	29.50	--	0.491	--	--	--
2E 38.5	29.90	8.60	0.500	0.716	1.43	0.000
3E 55.8	28.21	27.59	0.470	2.299	4.89	1.359
4E 50.4	22.18	28.22	0.370	2.351	6.35	1.611

Another materials balance analysis was run on a set of fabrics studied earlier. From the fixed weight gain and nitrogen analyses of the fabrics, the methylene content and formaldehyde urea ratios were calculated by difference. It was assumed in these calculations that the "combining weight" of formaldehyde in all the possible reactions is 12 and that the maximum mols of CH_2O that could combine with urea is 2:

1\. $NH_2CONH_2 + CH_2O \text{ ——— } -NHCONHCH_2- + H_2O$

$$60 + 30 \text{ ——— } 60 + 12 + 18$$

2\.



$NH_2CONH_2 + CH_2O \text{ ——— } -\underset{\substack{|\\ CH\\ |}}{N} - CO - \underset{\substack{|\\ CH\\ |}}{N} - + H_2O$

$$60 + 2(30) \text{ ——— } 60 + 2(12) + 36$$

3\. $2\ ZOH + NH_2CONH_2 + 2\ CH_2O \text{ ——— } ZOCH_2NHCONHCH_2OZ + 2\ H_2O$

$$X + 60 + 2(30) \text{ ——— } X + (60 + 2 \times 12) + 36$$

4\. $ZOH + CH_2O \text{ ——— } ZOCH_2OZ + H_2O$

$$X + 30 \text{ ——— } (X + 12) + 18$$

Consequently, from these assumptions one could estimate how much formaldehyde had reacted with the cotton when the apparent CH_2O/urea ratio exceeded 2:1.

The results of these analyses are shown in Table 28. The B, C, D, and E sets refer to the 5, 10, 20, and 40% urea solutions applied, respectively. Only at the lower level set is there some symmetry in the results compared with those from the earlier absorption data. At all urea concentrations, CH_2O/urea ratios of both under 2 and over 2 were found. Consequently, varying degrees of resin formation, crosslinking and simple cellulose formalization must be occurring in these vapor reactions. In spite of the apparent heterogeneity of the reactions, the high wet and dry crease resistances shown earlier were fairly consistent, especially at the 5 and 10% urea levels. Whether the anomalies in CH_2O/urea ratios calculated are due to lack of uniformity of the vapor phase reaction or to other causes is presently not known.

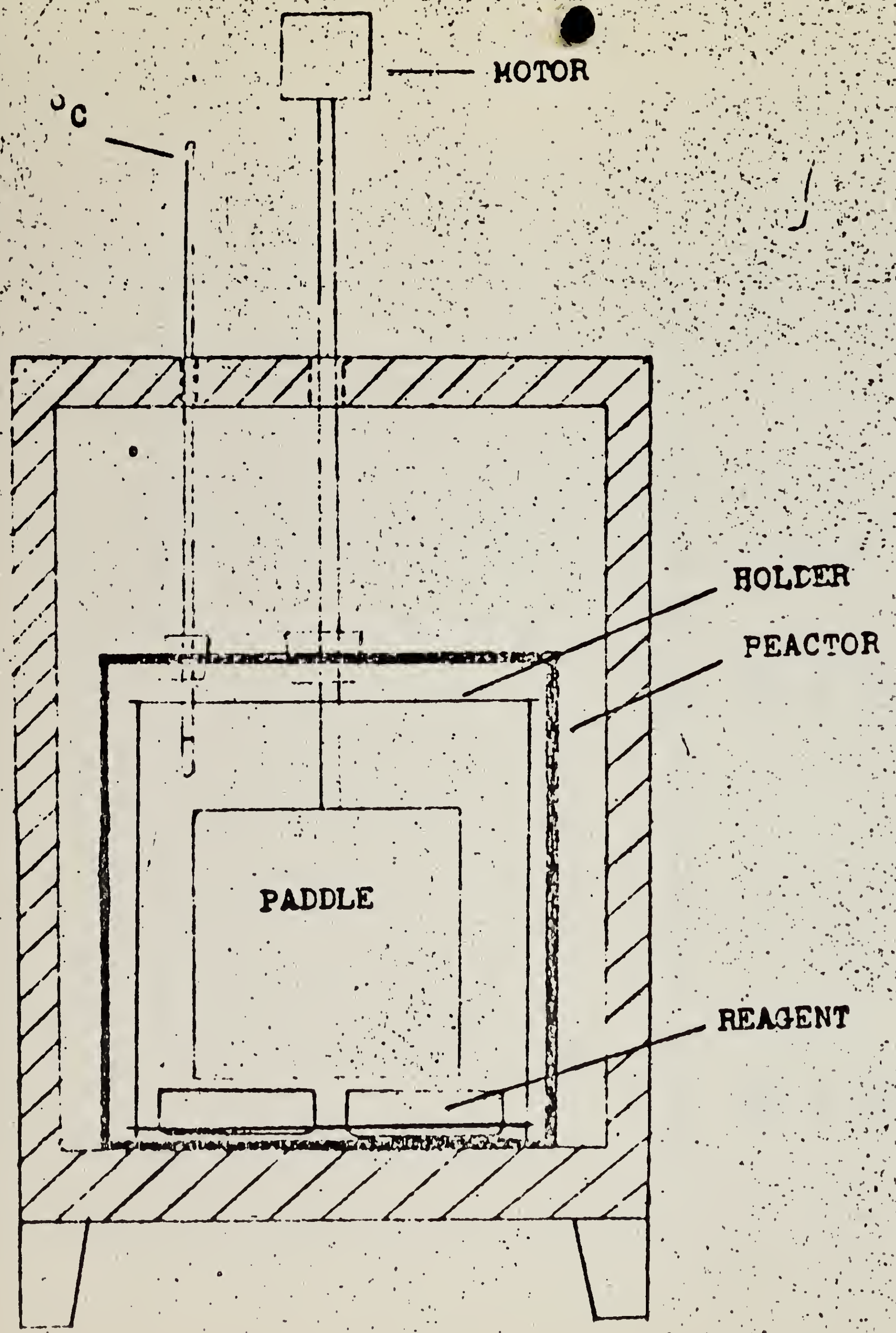
Table 29 shows a comparison of formaldehyde absorbed and reacted as $-CH_2-$ for both pure cotton and for cotton preimpregnated with urea. In the latter case, a higher amount of formaldehyde was absorbed and reacted in the fabric. Also, generally higher crease resistance was found in the urea samples. How much formaldehyde had reacted directly with the cotton in the urea samples is not known.

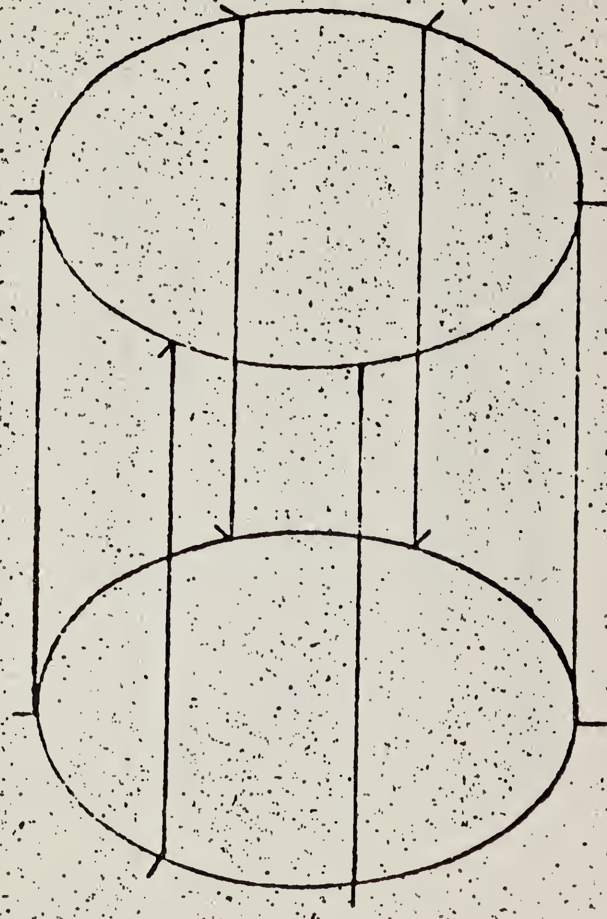
TABLE 29.--Vapor phase reaction of $CH_3OCH_2OH/HCOOH$ on cotton with and without urea preimpregnation (24 hours-scaled reactor-no postcure-scoured)

% Urea in Fabric	Reaction Temp. °C.	% CH_2O Absorbed	% Final Weight Gain ($-CH_2-$)	Warp Crease Resist. MCRA		Filling Tensile lbs./in.
				Wet	Dry	
None	30	1.81	-0.26	82	74	37
None	40	2.29	0.20	94	79	33
None	60	3.69	1.45	123	98	23
None	80	3.89	2.26	149	141	<15
3.70	30	6.58	1.78	136	94	26
3.04	40	6.74	2.13	132	117	26
3.76	60	7.89	3.08	138	137	20
3.57	80	10.03	6.03	138	115	17

The vapor phase reaction of formaldehyde donors on cotton preimpregnated with nitrogenous compounds can be studied in detail to obtain engineering data on how to accomplish the reaction in a reasonable time. Table 30 shows that under the present conditions used (80°C., 10 gms. cotton, 18 gms. Methyl Formcel, 30 gms. HCOOH) the reaction is slow.

These early tests had all been done in sealed one quart jars as the "reactor." In order to treat larger cloth samples, a 5-gallon polyethylene container was devised (Figure 6), and equipped with a stirring paddle, thermometer and glass beakers as reservoirs for the Methyl Formcel and Formic Acid liquids. This could be placed in an oven to carry out the vapor phase reactions at different temperatures. Here the cloth was wrapped around a circular stainless steel wire frame. It generally measured 12 x 34 inches. In order to test the uniformity of the reaction, a diagonal was drawn from the lower left hand to the top right hand side of the rectangular specimen. Crease test specimens were cut above and below this diagonal line to assess the uniformity of the treatment. In this case the cloth had been preimpregnated with 10% urea and dried. The reactor contained 180 gms. of 55% Methyl Formcel and 300 gms. of formic acid. The exposure was for 24 hours at 40°C. The uniformity of this treatment is shown by the data in Table 31 for two sets of samples.





FABRIC HOLDER

TABLE 30.--Rate of reaction of 10% urea preimpregnated cotton with $CH_3OCH_2OH/HCOOH$ vapors

Exposure Time At 80°C.	Crease Resistance - MCRA	
	Warp-Wet	Warp-Dry
1/4 hour	71	56
1/2 hour	73	79
1 hour	91	104
2 hours	130	96
4 hours	141	135
8 hours	144	112
16 hours	145	104

TABLE 31.--Warp crease resistance in different locations of vapor exposed cotton

	Warp Crease Recovery Angle			
	Sample A		Sample B	
Position	Dry	Wet	Dry	Wet
1. Top	116	143	141	136
2. Top	109	138	137	136
3. Top	110	141	136	152
4. Top	115	147	133	143
5. Top	123	152	143	147
1. Bottom	135	153	155	156
2. Bottom	112	153	135	142
3. Bottom	140	145	133	143
4. Bottom	135	157	129	148
5. Bottom	136	142	140	150

These results follow previous patterns, i.e., very high wet and dry crease resistance is produced by the vapor treatment. The wet values again are generally higher than the dry. This is not common with normal pad treatments with preformed urea-formaldehyde resins.

The larger reactor is now being used to prepare large enough pieces of cotton for more detailed examination of fabric properties. It was hoped that the in situ resin formation might yield better mechanical properties than normal resin pad applications. Preliminary tests with the urea case are shown in Table 16. Here the cotton was padded through the urea solutions and dried 10 min./105°C. Then they were placed in the reactor for 24 hours at 50°C., removed, conditioned, and tested.

The results in Table 32 indicate that either insufficient catalyst or Methyl Formcel were in the vapor phase. Note that the crease resistance performance decreased as the urea content of the fabric increased. The results indicate that a more detailed examination of reagent vapor concentrations must be made to balance the concentration of base in the fabric. While tensile strength losses appear to be normal for the degree of crease resistance produced the flex abrasion if much higher than that usually obtained in crosslinking treatments. Note the very high value found in the 20% urea sample! This behavior will be examined for cases other than urea.

TABLE 32.--Mechanical properties of vapor phase reacted cottons (urea preimpregnation + $CH_3OCH_2OH/HCOOH$ vapors)

% Urea In Sample	W+F Crease Recovery		Tensile-Lbs./in.		Stoll Flex Cycles(2:1/2)
	Dry	Wet	W	F	Warp
Untreated	142	107	64	42	355
20%	208	249	53	36	957
10%	288	277	31	21	261
5%	302	300	31	22	258

Cyclic Ureas and Other Reactants

In view of the success of forming resins and obtaining high crease resistance values in urea preimpregnated cotton, it was decided to examine a similar technique with nonresin forming materials such as:

Ethylene urea (EU)
Ethyl carbamate (EC)
Formamide (F)
Ethyl triazone (TR)
Dihydroxyethyleneurea (DHEU)

All of these compounds have two active hydrogens that can form dimethylol adducts which in turn can react with the cotton cellulose:

$$\text{H-R-H} + 2\ \text{CH}_2\text{O} \longrightarrow \text{HOCH}_2\text{-R-CH}_2\text{OH}$$

$$2\ \text{ZOH} + \text{HOCH}_2\text{-R-CH}_2\text{OH} \longrightarrow \text{ZOCH}_2\text{-R-CH}_2\text{OZ} + 2\ \text{H}_2\text{O}$$

In the first experiment, cotton fabrics were impregnated by padding with 10% solutions of these various compounds and dried for five minutes at 250°F. Then they were exposed to vapors of Methyl Formcel and HCl as had been done in the urea case. The results of weight gain, formaldehyde absorbed, fixed resin, and crease resistance obtained are shown in Tables 33 through 35. The ethyl carbamate and formamide samples showed only small weight gains after the first drying step, indicating volatile losses.

Further weight loss occurred with these during the vapor phase formaldehyde treatment. With the other compounds, weight gain results comparable to the urea case were found. Again higher wet than dry crease resistance was obtained. Also the high level of wet crease resistance found is not normal for the conventional pad-dry-dure application of preformed dimethylol analogs of these compounds.

TABLE 33.--Resin formation through vapor phase reaction[1] of CH_3OCH_2OH/HCl with various nitrogenous resin intermediates (RI) preimpregnated cotton

RI Soln. Applied[2]	% RI Deposited	% HCHO Absorbed	Mole % RI	Mole % HCHO	Ratio F/RI
Urea	9.43	4.07	0.157	0.136	0.9
EU	8.43	1.92	0.098	0.064	0.7
EC	[3] 2.27	-	-	-	-
F	[4] 1.23	-	-	-	-
TR	9.09	2.31	0.072	0.077	1.1
DHEU	9.28	3.52	0.079	0.177	2.2

[1] 24 hours/50°C.; 18 g. Methyl Formcel + 5 ml. HCl.

[2] 10% solids by weight in bath.

[3] Loss to 0.41% during vapor reaction.

[4] Loss to 0.51% during vapor reaction.

TABLE 34.--Resin formation through vapor phase reaction of CH_3OCH_2OH/HCl with various nitrogenous resin intermediates preimpregnated cotton

RI Soln. Applied	Initial Weight Gain-%	Fixed Resin-% Dry Cure
Urea	13.5	13.0
EU	10.4	9.7
EC	0.4	0.4
F	0.5	0.1
TR	11.4	8.0
DHEU	12.8	10.0

TABLE 35.--Resin formation through vapor phase reaction CH_3OCH_2OH/HCl with various nitrogenous resin intermediates preimpregnated cotton

RI Soln. Applied	Warp Crease Resistance	
	Wet	Dry
Urea	152	150
EU	152	138
EC	124	97
F	126	100
TR	135	118
DHEU	153	147

In a second experiment, the catalyst was varied. Here 1% NH_4Cl was impregnated in the cotton along with the resin or reactant intermediate. Then the dried cotton was exposed to the vapors of Methyl Formcel only. Table 36 shows the amount of formaldehyde absorbed by this technique. Again, loss of reagent occurred with the ethyl carbamate and formamide during drying. Table 37 shows the total weight gain and fixed resin found after a postcure and extraction. Table 38 shows the crease resistance found. The urea did not perform well with this catalysis. Very high wet and dry crease resistance was found with the remaining compounds, and especially with ethyl carbamate and formamide; this, in spite of the low weight gain produced by the two compounds.

Two nonvolatile carbamic acid esters have recently been commercially introduced: hydroxyethyl carbamate and methoxyethyl carbamate.

Hydroxyethyl carbamate-----------$HOCH_2CH_2OCONH_2$
Methoxyethyl carbamate-----------$CH_3OCH_2CH_2OCONH_2$

When combined with about 2.5 moles of formaldehyde, these yield highly chlorine resistant cotton finishes.

TABLE 36.--Resin formation through vapor phase reaction[1] of CH_3OCH_2OH/NH_4Cl with various nitrogenous resin intermediates preimpregnated cotton

RI soln. Applied[2]	% RI Deposited	% HCHO Absorbed	Mole % RI	Mole % HCHO	Ratio F/RI
Urea	10.47	1.60	0.174	0.053	0.3
EU	9.39	2.99	0.109	0.100	0.9
EC	2.77	0.27	0.031	0.090	2.9
F	2.20	1.08	0.049	0.036	0.7
TR	9.01	2.99	0.071	0.100	1.4
DHEU	9.36	2.14	0.079	0.071	0.9

[1] 24 Hours/50°C.

[2] 10% Solids by weight in bath.

TABLE 37.--Resin formation through vapor phase reaction of CH_3OCH_2OH/NH_4Cl with various nitrogenous resin intermediates preimpregnated cotton

RI Soln. Applied	Initial Weight Gain-%	Fixed Resin-% Postcured
Urea	12.07	6.4
EU	12.38	10.3
EC	3.04	1.6
F	3.28	1.9
TR	12.00	10.0
DHEU	11.50	9.0

TABLE 38.--Resin formation through vapor phase reaction of CH_3OCH_2OH/NH_4Cl with various nitrogenous resin intermediates preimpregnated cotton

RI Soln. Applied	Warp Crease Recovery	
	Wet	Dry
Urea	110	99
EU	151	149
EC	169	148
F	155	143
TR	143	141
DHEU	143	144

In our work, the hydroxyethyl carbamate ester was used at 10% concentration + 1% NH_4Cl as a dried-in catalyst to preimpregnate and dry 100% Delta Pine Cotton fabrics. Then these fabrics were exposed in the vapor reactor to vapors of methanol hemiformal. The Methyl Formcel reservoir was kept at 60°C., and the cloth reaction chamber was kept at 80°C. The N_2 flow rate was controlled by a Tube #0532-150, 10 lbs./in.^{2} on #8 setting of the regulator valve. Table 39 shows the results of MCRA values obtained on these samples exposed for different periods of time. Only slight creaseproofing was obtained by this catalyst preimpregnation technique at the temperature-time cycles used.

Vapor Catalyzed Carbamate Finish

Attempts were, therefore, made to use the Methyl Formcel-Formic Acid vapor catalyzed procedure to obtain higher yields. Here, the Delta Pine printcloth was impregnated only with 10% solution of hydroxyethyl carbamate and dried 5 min./250°F. The samples were exposed simultaneously for 4 hours at 50°C. to the vapors of the following reactant-catalyst mixtures:

A. 100 gms. Methyl Formcel
   50 gms. Formic Acid

B. 100 gms. Methyl Formcel
   100 gms. Formic Acid

TABLE 39.--Vapor phase application of methanol hemiformal to hydroxyethyl carbamate-NH_4Cl preimpregnated cotton

Exposure Time-Hrs.	MCRA (W+F)	
	Wet	Dry
1/2	146	129
1	173	158
2	166	160
4	184	178

C. 100 gms. Methyl Formcel
200 gms. Formic Acid

D. 100 gms. Methyl Formcel
400 gms. Formic Acid

These solutions were divided in half and placed into two separate evaporating dishes in the reactor. Vapor circulation was maintained by operating the paddle stirrer. At the end of the exposure period, the chamber was opened, the cloth samples removed washed in 0.5% Tide solution 10 min./120°F., rinsed several times, extracted and frame dried 5 min./250°F. The following weight losses were found (evaporation leaks plus fiber reaction):

Solutions	Original Weight	Weight Loss
A-1	73.0 gms.	23.3 gms.
A-2	75.2 gms.	22.5 gms.
B-1	100.0 gms.	40.5 gms.
B-2	100.0 gms.	40.1 gms.
C-1	149.3 gms.	33.5 gms.
C-2	151.7 gms.	35.5 gms.
D-1	250.0 gms.	73.7 gms.
D-2	250.0 gms.	63.1 gms.

Table 40 shows the effect which such vapor phase exposures produced on the fabric properties. As the ratio of formic acid to Methyl Formcel increased, improved wrinkle resistance was produced. Note the very high ratio of wet to dry wrinkle resistance values. Again these vapor phase exposures produced initially little or no change in abrasion resistance and a slight dip at higher wrinkle recovery values. But, in all cases, such abrasion resistance values were higher than those given by the pad-dry-cure method

The above experiments were repeated on vapor phase exposures of the same reaction mixtures, but now for four hours at 80°C. Similar postscouring and conditioning were done as before. The results are shown in Table 41. Here very high wrinkle resistance values were obtained, especially in the wet state. Again higher abrasion resistance was maintained at such levels than in conventional pad-dry-cure systems.

In view of the above results obtained in the closed chamber, further tests were made on the hydroxyethyl carbamate preimpregnated cotton inthe continuous flow reaction chamber. Here the dry 10% carbamate impregnated cotton fabrics were exposed to the Methyl Formcel/Formic Acid vapors (1:4) for varying times at 60°C. reservoir and 80°C. reactor temperatures. The fabric test results are summarized in Table 42.

TABLE 40.....Vapor phase crosslinking of hydroxyethyl carbamate preimpregnated cotton - 4 hrs./50°C.

Vapor Reactant Mixtures	MCRA (W+F)		Strip Tensile-lbs.		Stoll Flex Cycles-Warp	Wyzenbeek Abrasion-Warp
	Wet	Dry	Warp	Fill		
Untreated	149	160	56	38	670	-
A	180	170	51	36	685	942
B	211	193	48	34	645	1183
C	257	220	39	29	530	493
D	269	222	36	24	508	746

TABLE 41.--Vapor phase crosslinking of hydroxyethyl carbamate preimpregnated cotton - 4 hrs./80°C.

Vapor Reactant Mixtures	MCRA(W+F)		Stoll Flex	Wyzenbeek Abrasion-W
	Wet	Dry	W	
Untreated	149	160	670	-
A	261	218	599	571
B	285	246	322	839
C	285	255	275	559
D	303	270	264	396

TABLE 42.--Methyl Formcel/formic acid vapor treatments on 10% hydroxyethyl carbamate impregnated cotton fabric

Exposure Time-Hrs.	MCRA(W+F)		Stoll Flex Warp Cycles
	Wet	Dry	
1	183	185	793
1 1/2	243	209	731
2	293	248	592
4	299	275	450

These results confirm that the vapor phase catalysis of the carbamate preimpregnated cotton is preferred over the precatalyzed procedure. Note the very high wrinkle resistance-abrasion retention values obtained in these vapor treatments. This repetition of high wet and dry wrinkle resistance and high abrasion resistance retention appears to be a common phenomenon in crosslinking cotton in a vapor state under mild heat conditions. Since, in all such reactions, the cotton fibers are never baked nor dessicated during the crosslinking process, and since the crosslinking occurs in cotton containing 6-8% water and activated by formic acid vapors, the presumption is that here the cotton is being crosslinked in a swollen state as compared to pad-dry-cure methods. Consequently, any system that can further accentuate such crosslinking in a swollen state should produce further improvement in the abrasion resistance-wrinkle recovery ratio.

Cotton fabrics were preimpregnated with 10% solution of hydroxyethyl carbamate and dried. One set was exposed in the continuous flow 7-gallon reactor to vapors of 100# Methyl Formcel - 400# Formic Acid; the second set was exposed to vapors of Butyl Formcel. The same nitrogen flow was used in both cases. The Formcel-Formic Acid mix was kept at 60°C. The reactor temperature was at 80°C. Table 43 shows the results of fabric tests. The Methyl Formcel (higher vapor pressure) seems to have given more efficient wrinkle resistance at each exposure cycle than the Butyl Formcel (lower vapor pressure). Both produced high flex abrasion resistance.

TABLE 43.--Vapor phase reaction of methyl and butyl Formcels on 10% hydroxyethyl carbamate impregnated Deltapine cotton

1:4 Formcel-Formic Ratio	MCRA		Stoll Flex Cycles-W
	Dry	Wet	
Untreated	166	125	830
MFC - 1-1/2 Hrs.	243	209	731
MFC - 2 Hrs.	293	248	592
MFC - 4 Hrs.	299	275	450
Untreated	151	118	992
BFC - 1 Hr.	220	193	1190
BFC - 2 Hrs.	266	219	810
BFC - 4 Hrs.	281	247	589

Table 44 shows more complete tests done on the Butyl Formcel set of treated fabrics. The results are compared with those of a previously tested pad-dry-cure application of DMEU. It can be seen that the vapor exposure produces overall better abrasion resistance, tear strength and tensile strength than the DMEU control.

It is planned to explore a homologous series of alkanol hemiformals ($ROCH_2OH$) from methyl to ethyl, propyl, butyl, amyl, and methoxyethyl alkyls. Such studies should indicate whether the reaction in the vapor phase is strictly one of crosslinking:

$$Z - O(CH_2O)_n - Z$$

or whether alkoxymethyl side groups also form:

$$Z - OCH_2OR$$

If the latter reaction is also taking place, then there should be some dependence of fabric properties on the size of the R-group.

TABLE 44.--Vapor phase reaction of Butyl Formcel on 10% hydroxyethyl catbamate impregnated Deltapine cotton (reservoir at 60°C.; reactor at 80°C.)

Reaction Time-Hrs.	MCRA		Stoll Flex[1/] Cycles-W	Elmendorf Tear-Gms. (W+F)	Ravel Strip Tensile (W+F)	% Elongation at Break (W+F)
	Dry	Wet				
Untreated	151	118	992	816 + 480	55 + 33	10.0 + 21.6
1.0	220	193	1190	560 + 400	45 + 37	14.6 + 12.0
2.0	266	219	810	528 + 352	37 + 22	9.0 + 14.0
4.0	281	247	589	496 + 304	30 + 18	7.6 + 13.6
12% R-1/PDC	258	241	147	384 + 224	28 + 18	- -

[1/] 1-1/2 - 1/2 lbs.; blade #440.

Ethylene Urea Preimpregnations

Previous work with ehtylene urea preimpregnation of the Deltapine cotton fabric had shown this to be a useful means of producing a good vapor phase crosslinked cotton (Methyl Formcel/ Formic Acid System). This procedure was repeated on a 7 oz. twill pants fabric. The fabric was pretreated with 10% ethylene urea and 4% Aqualene N, a polyethylene latex, and dried. Then samples were exposed for various times and temperatures to vapors of different mixtures of Methyl Formcel-Formic Acid in the 5-gallon reactor.

The results are shown in Table 45. Effective dry and wet wrinkle resistance was produced in most cases. Note the very high surface abrasion resistance of the vapor phase treated samples compared to a "Koratron" type finish using:

18% Permafresh 183
3.6% Catalyst X-4
2.0% Polyethylene Softener

padded, dried 3 min./ 220°F, cured 5 minutes at 320°F.

Table 46 summarizes the results obtained on three sets of fabrics which had been preimpregnated with different concentrations of urea, ethylene urea and ethyl carbamate. The latter yielded little crease resistance (MCRA) under these conditions. The 5% and 10% urea and ethylene urea concentrations gave good crease resistance.

TABLE 45.--Vapor phase reaction of Methyl Formcel on 10% ethylene urea preimpregnated cotton twill

MFC/FA Ratio-Gms.	Time and Temperature	MCRA		Wyzenbeek Cycles-W
		Dry	Wet	
Untreated	-	141	121	6400
100/100	4 Hrs./80°C.	251	273	5440
100/200	4 Hrs./80°C.	270	305	2905
100/400	4 Hrs./80°C.	282	276	3161
100/100	8 Hrs./40°C.	229	234	3879
100/200	8 Hrs./40°C.	241	258	6423
100/400	8 Hrs./40°C.	256	238	4640
Koratron	3'/220/5'/320°F.	263	245	680

TABLE 46.--Vapor phase reaction of Methyl Formcel/Formic Acid on impregnated cotton (4 hrs./50°C.)

Nitrogen Base in Fabric	MCRA (W + F)	
	Wet	Dry
5% Urea	284	276
10% Urea	294	267
20% Urea	188	114
5% Ethylene Urea	258	227
10% Ethylene Urea	261	198
20% Ethylene Urea	264	212
5% Ethyl Carbamate	176	147
10% Ethyl Carbamate	204	151
20% Ethyl Carbamate	193	162

In Tables 47 and 48 are shown the results of comparisons between vapor phase formation of DMEU within the fibers versus conventional pad-dry-cure application of Rhonite R-1 plus 1.5% Catalyst H-7. Of special note is the difference in Stoll Flex Abrasion resistance of the two sets of fabrics. The vapor phase reactions appear to yield substantial improvement in flex abrasion resistance of the crosslinked cotton.

In Tables 49 and 50 are shown similar comparisons of a number of urea treated samples exposed for various times to vapors of Methyl Formcel/Formic Acid. Note the very high wet and dry crease resistance obtained in all samples. Note the values found with a conventional pad-dry-cure of different concentrations of a sesquimethylol urea composition. Although the difference in the two plateaus is not as sharp as for the ethylene urea case, it is nevertheless apparent that the two sets of fabrics have different properties.

TABLE 47.--Vapor phase reaction of Methyl Formcel/Formic Acid on ethylene urea preimpregnated cotton

(4 hrs./50°C.)

Pre-treatment % EU	MCRA(W+F)		Tensile lbs.		Stoll Flex Cycles Warp
	Dry	Wet	W	F	
5%	227	258	35	25	300
10%	198	261	41	26	336
20%	212	264	37	27	300

TABLE 48.--Conventional pad-dry-cure application of DMEU creaseproofing agent - 50% solids

% DMEU Product	MCRA (W+F)		Tensile lbs.		Stoll Flex Cycles Warp
	Dry	Wet	W	F	
0%	147	134	55	42	472
8%	255	230	31	23	183
12%	258	241	28	18	147
16%	273	259	27	20	139

TABLE 49.--Vapor phase reaction of methyl Formcel/formic acid on 10% urea impregnated cotton

Exposure Hrs./50°C.	MCRA (W+F) Dry	MCRA (W+F) Wet	Tensile Lbs. W	Tensile Lbs. F	Stoll Flex Cycles Warp
2	256	280	37	24	235
4	267	294	36	20	179
6	258	276	38	25	208
8	280	291	33	24	188
16	287	282	36	26	211
24	288	277	31	21	261

TABLE 50.--<u>Conventional pad-dry-cure application of methylol urea creaseproofing agent</u>

% Solids In Bath	MCRA (W+F) Dry	MCRA (W+F) Wet	Tensile Lbs. W	Tensile Lbs. F	Stoll Flex **Cycles** Warp
0	147	134	55	42	472
7.5	240	236	41	27	213
10.0	249	238	42	25	135
15.0	258	248	42	26	113
20.0	259	238	42	26	139
25.0	238	216	49	28	185
30.0	222	230	56	31	206

Propylene Urea Preimpregnations

Cotton fabrics were impregnated by padding with 5% propylene urea solutions in water, framed and dried 5 minutes/ 250°F. Then they were placed in the 5-gallon reactor containing a fixed amount of Methyl Formcel and Formic Acid in separate containers. Two pieces of cotton fabric (12" x 34") were pinned around the tubular sample holder. Vapor exposures were made both at 50°C. and 80°C. for four hours. To compare the vapor phase exposures to a conventional pad-dry-cure system, the same fabrics were treated with increasing concentrations of dimethylol propylene urea (Fixapret PH and Catalyst H-7). The fabrics were dried and then cured 5 min. at 300°F.

The results of these tests are shown in Table 51. The conventional pad-dry-cure system produced the normal very high loss in flex abrasion resistance, surface abrasion resistance, and tensile strength. The 50°C. exposures to varying amounts of Methyl Formcel/Formic Acid yielded the best overall fabric properties. Note the very high abrasion resistance values by both tests. Also, note the higher retention of tensile strength. The 80°C. exposure produced even higher wrinkle resistance values. But even here, the overall strength and abrasion resistance properties were better than those of the dimethylol propylene urea treated samples.

These results again demonstrate that the low temperature vapor phase crosslinking of cotton, swollen with its normal 6-8% moisture content, produces better overall strength properties than resin curing systems.

In the above experiment with vapor phase reactions on propylene urea impregnated cotton, several other observations were made. Table 52 shows the results of weight gain tests on the two cotton samples placed as an inner and an outer layer around the sample holder. It can be seen that good uniformity of treatment was found between the two layers.

Table 53 shows an attempt to follow the material balance of reagents during the exposure by measuring the amount of each reagent left in each container. Except that the higher temperature caused greater chemical loss, these results are not very definitive in assessing the value of a particular ratio of Methyl Formcel to Formic Acid. The average fabric weight gain at 80°C. seems to show a dependence on the chemical ratio.

TABLE 51.--Vapor phase reaction of Methyl Formcel on 5% propylene urea impregnated Deltapine cotton

Treatment Applied	MFC/HCOOH Ratio-Gms.	Time-Temperature	MCRA (W+F)		Abrasion Res.		Tensile-Lbs.	
			Dry	Wet	Stoll	Wyz.	W	F
Untreated	-	-	153	141	689	433	58	37
2.5% DMPU	-	5 Min./300°F.	242	224	465	319	36	23
5.0% DMPU	-	5 Min./300°F.	274	245	345	296	34	23
7.5% DMPU	-	5 Min./300°F.	301	270	164	209	31	17
MFC/HCOOH	100/50	4 Hrs./50°C.	247	249	589	990	37	30
MFC/HCOOH	100/100	4 Hrs./50°C.	276	252	695	625	39	30
MFC/HCOOH	100/200	4 Hrs./50°C.	278	259	872	1002	39	27
MFC/HCOOH	100/400	4 Hrs./50°C.	280	266	650	576	41	26
MFC/HCOOH	100/50	4 Hrs./80°C.	280	249	476	727	38	26
MFC/HCOOH	100/100	4 Hrs./80°C.	291	274	382	997	34	25
MFC/HCOOH	100/200	4 Hrs./80°C.	292	280	392	1028	31	22
MFC/HCOCH	100/400	4 Hrs./80°C.	283	276	400	552	30	17

TABLE 52.--Percent weight gain of two layer fabric exposures

Reaction Ingradients Gms.	4 Hrs. Exposure Temperature	Cloth Layer	
		Outer	Inner
100 MFC/50 FA	50°C.	12.0	10.2
100 MFC/100 FA	50°C.	4.7	5.5
100 MFC/200 FA	50°C.	6.2	5.6
100 MFC/400 FA	50°C.	5.2	4.7
100 MFC/50 FA	80°C	0.3	0.4
100 MFC/100 FA	80°C	1.4	2.7
100 MFC/200 FA	80°C	2.3	3.4
100 MFC/400 FA	80°C	4.5	3.9

TABLE 53.--Material balance in vapor phase crosslinking of 5% propylene urea impregnated cotton

Reaction Ingredients Gms.	4 Hrs. Exposure Temperature	% Weight Loss		% Weight Gain
		FA	MFC	
100 MDC/50 FA	50°C.	68	10	11.2
100 MFC/100 FA	50°C.	59	17	5.1
100 MFC/200 FA	50°C	15	11	5.9
100 MFC/400 FA	50°C	-	-	5.0
100 MFC/50 FA	80°C.	98	63	0.3
100 MFC/100 FA	80°C.	100	80	2.1
100 MFC/200 FA	80°C.	100	47	2.9
100 MFC/400 FA	80°C.	24	33	4.2

Table 54 shows a comparison of properties produced when the two reagents were combined as one solution and where they were kept separate during the vapor exposure at 50°C. While differences were found, these results indicate the utility of combining the two ingredients into one solution. This is most important in simplifying the design of a commercial vapor phase oven.

TABLE 54.--Separate versus mixed chemicals (100 MFC-200 FA 50° C.)

Property	Separate	Mixed
Wgt. Gain #1	6.2	4.3
Wgt. Gain #2	5.6	4.0
Wgt. Loss	26%	40%
MCRA-Dry	278	274
MCRA-Wet	259	267
Stoll Flex	872	527
Wyzenbeek	1002	868
Tensile	39x27	36x24

Chlorosilane Curing of Resins

Vapor phase chlorosilane reactions on cotton yield high degree of silicone polymer formation within a few seconds' exposure at room temperature. Since hydrochloric acid is a byproduct of this reaction, it was postulated that a multifunctional finish might be produced. For example, if the cotton fabrics were to be previously impregnated with acid curing types of cellulose crosslinking agents and then passed into a reaction chamber containing chlorosilane vapors, then both silicone polymer formation and cellulose crosslinking might take place.

To test the above idea, samples of Deltapine cotton fabric were treated by pacding with a 10% solution of Rhonite R-1 (50% DMEU) and dried 5 minutes at 250°F. No catalyst was used. Pieces of this fabric were exposed to vapors of methyl hydrogen dichlorosilane. Monsanto Crease Recovery Angle tests (MCRA) were used to evaluate the degree of curing produced at room temperature. The results are shown in Table 55. These demonstrate that cellulose crosslinking was produced by the silane exposures on the DMEU impregnated cotton. Control samples without DMEU, and silane exposed, had MCRA values of only 182-189. The present results indicate the commercial possibility of devising a continuous process of resin impregnation and silane vapor exposures in a suitable reactor to obtain resin curing and water repellency in one run.

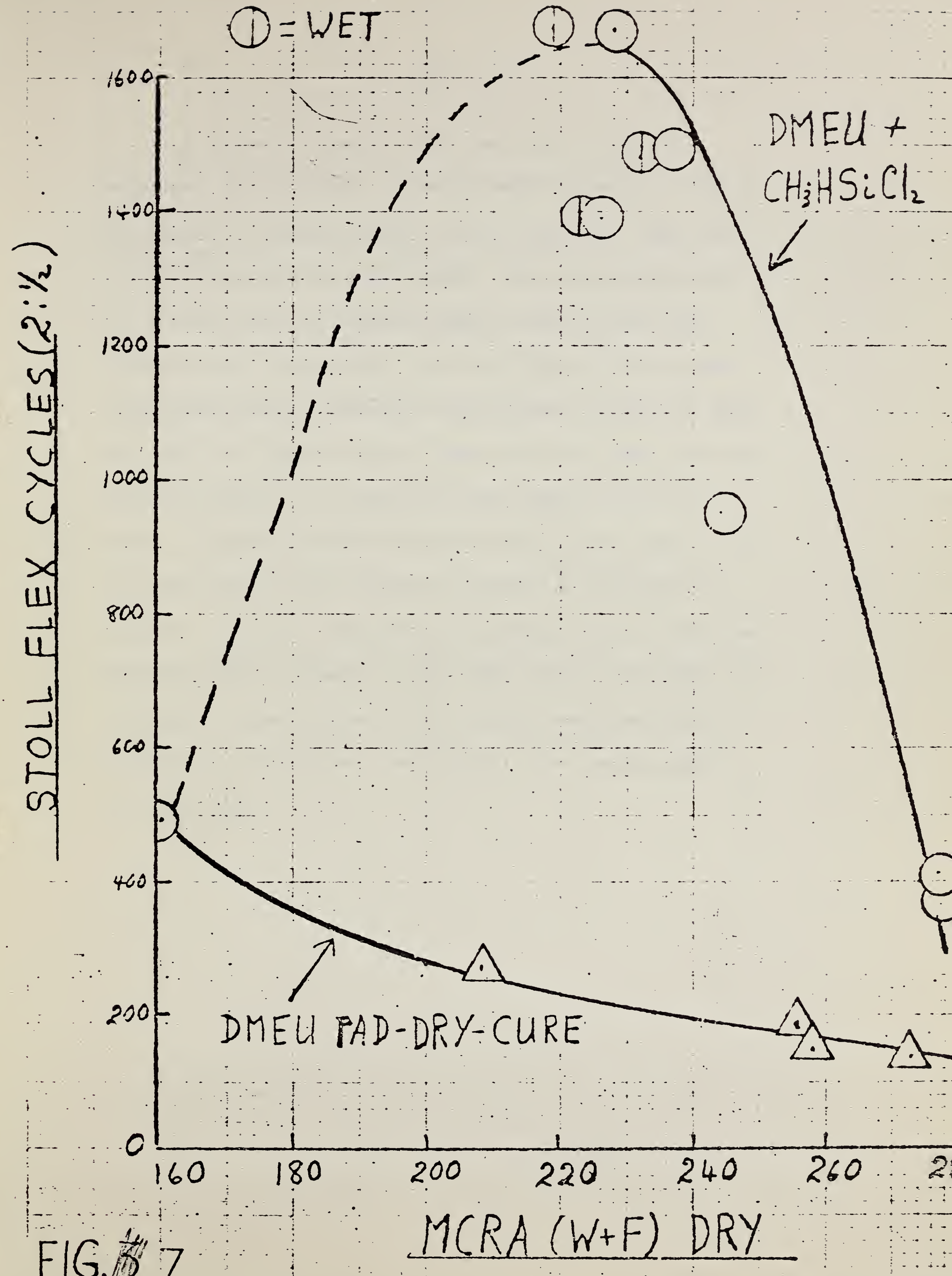
TABLE 55.--Room temperature vapor phase curing of DMEU by methyl hydrogen dichlorosilane[1]

Sample Exposure	Exposure Time	Spray Rating	Stoll Flex Cycles	MCRA Dry W	MCRA Dry F	MCRA Wet W	MCRA Wet F
Untreated	None	0	492	72	87	51	68
DMEU Only	None	0	560	72	77	58	80
Silane	15 sec.	100	1387	106	120	104	119
Silane	30 sec.	100	1679	110	118	96	123
Silane	60 sec.	100	1491	117	120	108	124

---

[1] N_2 Flow of 4000 cc/min.

The product shows crease resistance, water repellency and extremely high abrasion resistance. Longer time exposures have been completed and the total abrasion-crease resistance curve is shown in Figure 7. Here a comparison is made with the curve obtained by padding, drying, and curing 4, 8, 12, and 16% Rhonite R-1 and Catalyst H-7 as previously reported. Note the unusual shape of the vapor phase curve. Here the flex abrasion seems to rise as crease resistance improves; goes through a maximum, and then begins to fall. This is a remarkably different behaviour from that normally observed with all creaseproofing systems done by conventional padding methods.



① = WET
DMEU + CH_3HSiCl_2
DMEU PAD-DRY-CURE
STOLL FLEX CYCLES (2:½)
1600
1400
1200
1000
800
600
400
200
0
160
180
200
220
240
260
MCRA (W+F) DRY

FIG. 7

In order to confirm this behaviour, the above experiment was repeated on freshly DMEU-impregnated fabrics. The results are shown in Table 56 and Figure 8. Again the rise in flex abrasion was observed. Here we also measured the percent silicone polymer formed in and on the fiber (after solvent extraction). As can be seen, in the region of maximum abrasion resistance the silicone content is about the same. At higher exposure times and with larger silicone polymer formation, the abrasion curve begins to fall off again. A possible explanation for this reversal may lie in the fact that as more polymer is formed in the fiber and improves the fiber flexibility or extensibility, at the same time more HCl is formed to cause fiber tensile strength loss. It might be expected that if this second reaction could be eliminated or minimized, the abrasion curve maximum might be even higher.

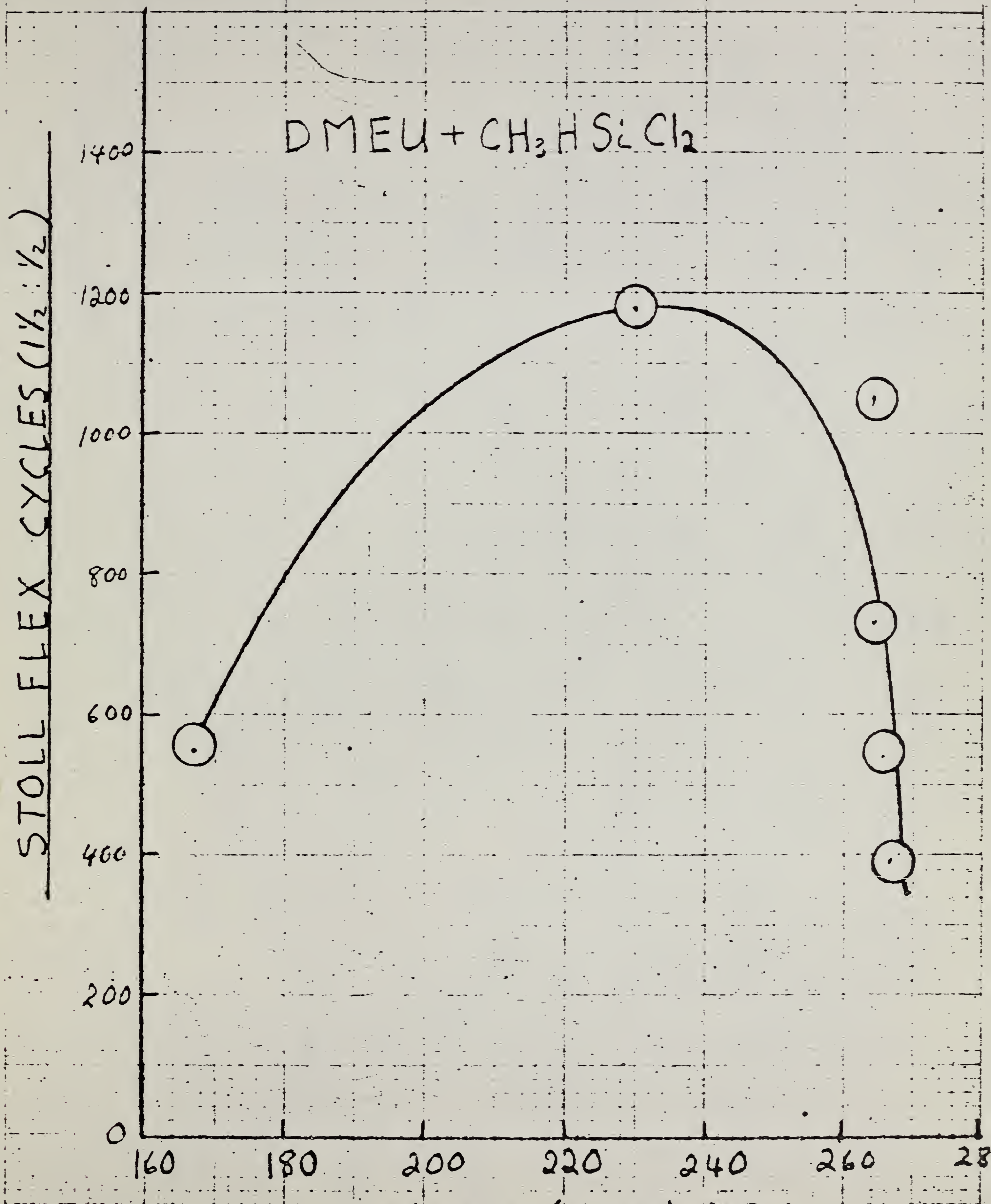

DMEU + CH_3HSiCl_2
STOLL FLEX CYCLES (1½ : ½)
1400
1200
1000
800
600
400
200
0
160
180
200
220
240
260
28
MCRA (W+F) DRY

FIG. # 8

TABLE 56.--Repeat run of cotton preimpregnated with 4% DMEU and then exposed to vapors of methyl hydrogen dichlorosilane at room temperature

Silane Exposure[1]	% Silicone Deposited	MCRA (W+F)	Stoll Flex (1 1/2: 1/2 lbs.)
			Cycles
None	None	167	551
15 Sec.	1.59	230	1180
30 Sec.	1.83	264	1053
60 Sec.	1.67	266	393
3 Mins.	7.80	264	738
5 Mins.	10.05	265	542

[1] 5 Minutes N_2 flush.

Some work on shorter exposure times is now underway. In one experiment, the five minutes nitrogen flush was eliminated. After the DMEU impregnated fabric had been exposed to CH_3HSiCl_2 vapors, it was removed from the reactor and immediately washed in a 1% sodium bicarbonate in isopropanol solution to neutralize any HCl formed and to deactivate the unused chlorosilane. Part of the results completed to date are shown in Table 57. In these shorter exposure times, the silicone polymer formation was greatly reduced. Note, however, that the flex abrasion resistance at the maximum was now increased over four folds of that of the untreated fabric. This possibly indicates less HCl fiber damage. Further balance of exposure times, abrasion resistance and curing efficiency is necessary to optimize all fabric properties.

TABLE 57.--Shortened chlorosilane exposures (No N_2 flush) on cotton preimpregnated with uncatalyzed DMEU-4%

Silane Exposure Time-R.T.	% Silicone Deposited	MCRA (W+F)	Stoll Flex (1 1/2: 1/2)
			Cycles
None	0.00	165	892
15 Sec.	0.00	214	1755
30 Sec.	0.00	217	3655
60 Sec.	0.51	230	4019
3 Mins.	0.70	210	3175
5 Mins.	1.54	222	3046
30 Sec.1/	0.00	224	3302
30 Sec.1/	0.61	221	2674
30 Sec.1/	0.00	238	2975
4% DMEU2/	-	265	575
5.6% DMEU2/	-	279	328
7.2% DMEU2/	-	292	276

1/ With 4%, 5.6%, 7.2% DMEU, respectively.

2/ Pad, dry, cure control with Catalyst H-7.

Precured DMEU + Chlorosilane Vapors

In order to determine whether simple surface silicone polymer formation was responsible for the improved abrasion resistance, a set of cotton fabrics which had been pretreated by pad, dry and curing with different solids concentrations of DMEU was exposed to CH_3HSiCl_2 vapors. The influence of the chlorosilane vapor treatment is shown by the data in Table 58. The posttreated samples contained from 7-9% silicone polymer, yet the flex abrasion resistance was not very different from that of the original samples. These results indicate that the simultaneous <u>in situ</u> crosslinking and silicone polymer formation as previously done must be affecting the cotton fibers in an entirely different manner from that of the two-step procedure. Again, the possible reasons may be the low temperature used in the vapor phase crosslinking and the location of the polymer in the fibers.

TABLE 58.--Influence of methyl hydrogen chlorosilane vapors on precured DMEU treated cotton

% DMEU[1/] Dry and Cure	Silane[2/] Posttreat	MCRA (W+F)	Stoll Flex (1 1/2: 1/2 lbs.)
			Cycles
Untreated	None	136	588
1.5%	None	218	294
3.0%	None	250	382
5.0%	None	272	278
1.5%	Yes	232	225
3.0%	Yes	238	363
5.0%	Yes	261	449

[1/] 80% Wet pickup; 1.25% Catalyst H-7; dried 5 min./250° F.; cured 5 min./300° F.

[2/] 1 Minute exposure, 5 minutes N_2 flush at R. T.

Preformed Silicone Polymers with DMEU

Similar tests of the influence of polymer location on flex abrasion performance were made by applying to cotton various padding mixes containing commercial preformed silicone polymers used for water repellency. The results at the 10% DMEU product (50%) level are shown in Table 59 and compared to the vapor treatment. While these high silicone concentrations produced improved flex abrasions, the results were not as high as those shown in Table 57 for the short chlorosilane exposures. Other pad, dry, cure tests with high silicone polymer solids at low crosslinking levels also produce a maximum in the flex abrasion curve. But, again, this is of a lower order from that produced by the chlorosilane vapor/DMEU combination.

TABLE 59.--DMEU treatments with and without silicone polymer additives versus vapor treatment

Treatment Applied[1]	MCRA (W+F)	Stoll Flex Cycles
A) 10% DMEU) 1 1/4% H-7) Dry & Cure)	272	278
B) 10% DMEU) 1 1/4% H-7) 6% Decetex 104) 1.2% Cat. X-21) Dry & Cure)	298	443
C) 10% DMEU) 1 1/4% H-7) 20% Decetex 104) 4% Cat. X-21) Dry & Cure)	311	404
D) Untreated	136	388

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[1] All on product basis; 80% wet pickup; dry 5'/250° F.; cure 5'/300° F.

Vapor Phase Grafting

Hydroxyethylation Grafts

Some experiments were undertaken on the vapor phase hydroxyethylation of cotton fabrics under various reaction conditions. With high concentration of NaOH catalyst and long exposure times, the cotton became water soluble at over 20% ethoxylation with ethylene oxide gas. None of these results indicated whether the graft was one of mono- or polyhydroxyethylation of the cellulose:

$$\text{Cell} - \text{O} - \text{CH}_2\text{CH}_2\text{OH} \qquad \text{or}$$

$$\text{Cell} - \text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$$

It had been observed that high NaOH concentrations caused gelatinization of the fibers and parchmentizing effects. With 10% NaOH fabric impregnation and ethoxylation, soft nongelatinized fabrics could be obtained. These fabrics were tested for various physical properties.

Table 60 shows the effect of ethoxylation grafts produced on the Deltapine cotton printcloth preimpregnated with 10% NaOH as catalyst. The exposures were in a Ben Venue sterilizer. Two sets were run: one to measure initial properties; the other to be used for posttreatment with creaseproofing agent. Slight shrinkage occurred under these ethoxylation conditions. Flex abrasion resistance was improved. Note the high wet wrinkle resistance produced at the 4-hour ethoxylation cycle.

That cotton fabrics pretreated with ethylene oxide have greater accessibility than untreated cotton and also show a better balance of abrasion resistance and wrinkle recovery is again demonstrated by the data in Table 61. The cotton fabric was ethoxylated by reaction with ethylene oxide using 10% NaOH as catalyst and a 4-hour room temperature exposure in the Ben Venue sterilizer. Following rinsing, souring and drying, the samples were padded through a solution of 10% Rhonite R-1 and 1.5% Catalyst H-7, frame dried and cured for 5 minutes at 300° F. Note the much higher wrinkle recovery values obtained in the ethoxylated fabric. The sample treated with NaOH but not ethoxylated behaved as the unpretreated control.

TABLE 60.--Influence of ethoxylation grafts on cotton fabric properties (9 x 15 1/2" samples)

Hours of Ethoxy-lation	% Weight Gain	Final Sample Size	MCRA (W+F)		Stoll Flex Cycles-Warp
			Wet	Dry	
Untreated	0	9 x 15 1/2	140	134	738
0	0	9 1/2 x 15 1/8	171	116	981
1	1.44	9 x 14 3/4	165	120	908
2	3.59	9 1/2 x 14 3/4	176	120	1008
4	8.28	8 7/8 x 14	286	92	1042

TABLE 61.--Ethoxylated samples and crosslinking

(10% Rhonite R-1 + 1.5% H-7)

Pretreatment Applied	MCRA (W+F)	
	Dry	Wet
Untreated	141	117
None + R-1	260	238
NaOH + R-1	254	228
EO + R-1	283	274

Using the AATCC Static Absorption test, the results shown in Table 62 were obtained. These show that the cotton becomes more swellable in water as the degree of ethoxylation increases. Moreover, the 24-hour Moisture Regain increases proportionally to the degree of ethoxylation obtained. Such improved fiber swelling could be utilized to advantage in subsequent wrinkleproofing treatments.

Hydroxyethylation and Crosslinking

A series of cotton fabrics which had been hydroxyethylated as above in the vapor state (after washing out NaOH catalyst and souring with acetic acid) were subsequently treated by a conventional pad-dry-cure procedure with 10% Rhonite R-1 + 1.5% Catalyst H-7. The results of wet and dry wrinkle resistance tests and Stoll Flex Abrasion tests are shown in Table 63.

TABLE 62.--Influence of vapor phase ethoxylation on fiber swelling

Hours of Ethoxylation	% NaOH Catalyst	% H_2O Absorption	% Moisture Regain
0	10	65.4	6.02
2	10	80.4	7.65
4	10	88.0	7.83
0	15	70.5	7.59
1	15	70.9	8.88
2	15	99.5	9.84
4	15	116.8	11.50

TABLE 63.--Hydroxyethylation grafts and crosslinking of cotton: 10% R-1 + 1.5% Catalyst H-7

% Graft From Ethylene Oxide	MCRA (W+F)		Stoll Flex Cycles-Warp
	Wet	Dry	
Untreated	140	134	738
Resin Treated Only	240	258	557
0% Graft + Resin	258	259	911
1.64% Graft + Resin	270	239	920
3.30% Graft + Resin	293	237	919
7.45% Graft + Resin	307	288	751

The results shown in Table 63 indicate a remarkable improvement of wrinkle resistance and abrasion resistance at the 7.45% ethocylation level. Moreover, note the high wet wrinkle resistance produced by the resin finish as ethoxylation increased. Such results point to the practical possibility of separately, or consecutively, hydroxyethylating cotton and crosslinking it with conventional resins or vapor phase systems to produce high strength fabrics.

Acrylate Grafts and Crosslinking

Various acrylate monomers, reacted with cotton by the ceric ion procedure, produce various degrees of improvement in wrinkle recovery and abrasion resistance. Attempts have now been made to use the vapor phase acrylate graft to modify cotton prior to crosslinking. Here, butyl acrylate monomer was grafted to the Deltapine fabric to give weight gains of 1.57%, 7.16% and 15.6%. Such fabrics were subsequently treated by padding, drying and curing with 10% Permafresh 183 and Catalyst X-4. Drying was at 5 min./250°F. and curing was at 5 min./300°F. In such padding, the acrylate grafted samples were difficult to wet-out even when using wetting agents. The results of these tests are shown in Table 64. Here, again, the acrylate pregrafts yielded a better abrasion-wrinkle recovery ratio than is usually found in conventional wrinkleproofing finishes. Attempts are now being made to combine grafting and crosslinking into one vapor phase reaction.

TABLE 64.--Butyl acrylate grafted cotton followed by crosslinking with Permafresh 183

% Acrylate Graft	Dry MCRA (W+F)	Stoll Flex Cycles-Warp
Untreated	171	707
No Graft	261	324
1.57% Graft	246	298
7.16% Graft	249	1710
15.60% Graft	256	600

Chlorosilane Grafts and Crosslinking

Cotton fabrics preimpregnated with uncured crosslinking agents can be creaseproofed by exposure to vapors of chlorosilane monomers. Presumably here, the grafts on the cellulose were given by the silanic esters, and the liberated HCl caused the crosslinking agent to react with the cellulose to produce wrinkle resistance. Since moisture is important in the chlorosilane reaction with fibers, an experiment was carried out to learn the influence of moisture on dimethylol urea preimpregnated cotton and resin fixation. Here the cotton fabrics were padded with a 10% solution of Rhonite R-1 (50% DMEU) at 80% wet pickup and dried 5 min./250°F. Then they were conditioned in ovens or over salt solutions to give 0-1%, 4.5-5.0% or 10-11% moisture prior to insertion into the vapor reactor. After the appropriate exposure to vapors of methyl hydrogen dichlorosilane, the samples were flushed with nitrogen for 10 minutes, removed from the chamber, washed with 1% $NaHCO_3$ in 80% IPA-20% H_2O, rinsed in water and dried 5 min./220°F. The total weight gains of cured DMEU + silicone graft are shown in Table 65. These results show that both the time of reaction and the fabric moisture content are most important in this simultaneous graft-crosslinking reaction. Moisture, however, is absolutely necessary in the process. Little or no resin fixation or crosslinking was shown in the samples with 0.1% moisture content. Previously, it was

demonstrated that the chlorosilane vapor exposure on cotton preimpregnated with cellulose crosslinking agents could be an important method of obtaining highly abrasion resistant and crosslinked cotton fabrics. This is further demonstrated by the data in Table 65.

TABLE 65.--**Influence of moisture content on silane grafts and crosslinking of cotton fabrics**

% Moisture In Samples		% Weight Gain	MCRA (W+F)		Grab Tensile-lbs.		Stoll Flex Cycles-Warp
			Wet	Dry	Warp	Fill	
0-1	15 sec.	0	227	211	47	33	805
0-1	60 sec.	0	196	222	43	34	3068
0-1	300 sec.	0	234	224	46	33	2142
4.7	15 sec.	0.67	162	165	64	51	1875
4.4	60 sec.	2.93	242	245	37	28	1414
5.5	300 sec.	4.34	244	258	32	26	998
10/11	15 sec.	1.30	255	244	39	25	2735
10/11	60 sec.	4.75	278	269	27	19	2245
10/11	300 sec.	8.76	287	264	20	14	370
Pad-Dry-Cure		-	247	274	37	25	324

Chlorosilane Grafts and Methyl Formcel

Since the chlorosilane-cellulose crosslinking systems previously reported with DMEU and other nitrogen based compounds seemed to be of practical value for vapor phase crosslinking, attempts were made to use methanol hemiformal preimpregnated cotton. It was realized that because of the low boiling point of this product (80-82°C.), little of it might be left on the fabric after padding and drying. Nevertheless, enough cellulose hemiformal ($ZOCH_2OH$) might be formed to be of use during the chlorosilane exposure. To test this idea, cotton fabrics were padded first with:

20% Methyl Formcel (55%)
1% $NaHCO_3$
79% Water

and dried 5 min./200°F. Exposures to the chlorosilane vapors in the reaction chamber were made within two hours. The fabric moisture content was estimated to be 6-8%. Following the usual exposure, flushing and alcoholic alkali rinsing previously described, the samples were dried and later tested. The results are shown in Table 66. Little weight gain was produced. Some increase in wrinkle resistance was found and a great improvement in flex abrasion resistance was given. Because of the high volatility of the Methyl Formcel, little crosslinking was produced. Again, however, a positive slope was obtained in the abrasion resistance-wrinkle recovery curve.

TABLE 66.--Methyl hydrogen dichlorosilane exposures on Methyl Formcel treated cotton

Reaction Time-Seconds	% Weight Gain	MCRA (W+F)		Stoll Flex Cycles-Warp
		Wet	Dry	
0	0.00	130	144	761
15	1.28	169	175	1363
30	1.38	174	186	1204
60	1.21	181	199	1047
180	1.84	168	194	1742
300	0.00	174	197	1795
600	0.91	182	201	1796

Chlorosilane Grafts and DMEU

It was postulated that if the chlorosilane exposure on DMEU preimpregnated cotton could be moderated to minimize HCl damage to the cellulose, even higher abrasion resistance might result from this grafting-crosslinking modification of cotton. That better tensile and abrasion resistance is possible, is shown in Table 67. Here, in the lower case, the normal 5 minutes "N_2 flush" was given to each sample. The above set represents one where the flush cycle was eliminated and the samples were quickly neutralized in alcoholic alkali solutions. Note the tremendous increase in flex abrasion resistance and also in tensile strength properties of the cotton fabrics. Again, both abrasion curves go through a maximum, which is a different behaviour from the common creaseproofing curve obtained by conventional resin curing.

Vapor Phase Permanent Press

The results which have been obtained to date on various vapor phase crosslinking reactions on cotton fabrics indicate the possibility of developing a practical vapor phase creaseproofing process for garment treatments. At least two techniques appear very practical:

TABLE 67.--Tensile losses in 4% DMEU preimpregnated cotton exposed to methyl hydrogen dichlorosilane

Silane Exposure at R. T.	Nitrogen Flush 5 Mins.	Stoll Flex Cycles Warp	Tensile Strength Lbs./Inch	
			Warp	Fill
Untreated	None	892	63	45
15 Sec.	None	1755	42	20
30 Sec.	None	3655	40	31
60 Sec.	None	4019	37	28
3 Min.	None	3175	31	27
5 Min.	None	3046	35	25
Untreated	Yes	551	61	46
15 Sec.	Yes	1180	26	21
30 Sec.	Yes	1053	20	16
60 Sec.	Yes	393	21	15
3 Min.	Yes	738	21	15
5 Min.	Yes	542	17	15

1. Fabrics containing softeners, stiffening agents or other hand modifiers are cut, sewn into a garment, steam pressed into shape, and then are exposed in a chamber to vapors of a crosslinking agent and catalyst. The simplest system we have found so far is a combination of Methyl Formcel and Formic Acid. After the exposure and crosslinkage formation, the garments must be air-flushed or chemically neutralized in a vapor step to eliminate unreacted reagents.

2. A second procedure would be to impregnate fabrics in a finishing plant with various formaldehyde reactive compounds such as propylene urea, ethylene urea, hydroxyethyl carbamate, etc. After reaching the garment plant, the garments would be exposed as before to vapors of Methyl Formcel-HCOOH. Depending on chlorine resistance, durability, costs, weight, and other requirements, various nitrogenous compounds could be used. Also, other functional finishing agents could be employed.

A vapor phase permanent press process for 100% cotton garments could offer the following actual or potential advantages over existing processes:

1. Ability to operate outside of restrictive precure and postcure patents.

2. Higher strength and abrasion resistance in 100% cotton fabrics than are given by other methods.

3. Ability to treat white cotton garments with completely chlorineproof and permanent crosslinking agents.

4. No problems of storage stability from the finishing plant stage to the final garment making.

5. Lower operating costs of the garment curing ovens or vapor reactors since it is contemplated to use temperatures below 100°C. instead of the 160-180°C. now in use.

Before a practical garment treating machine can be designed and built, it will be necessary to undertake more extensive organic, physical, and chemical engineering studies than have been accomplished to date.

Garment Treatments

100% Cotton Brassieres

Based on the information previously developed from vapor phase treatments of the 100% Deltapine cotton fabric, a series of tests were made to prepare 100% cotton durable press garments. These preparations were intended to demonstrate the practical utility of garment treatments and to test crosslinking uniformity by dyeing tests.

One garment which was treated was a 100% cotton brassiere. The 5-gallon reactor contained 100 grams of 55% Methyl Formcel and 200 grams of Formic Acid mixed together and then placed in two separate beakers. The exposure was for 4 hours at 80°C. The so-treated garment and one untreated brassiere were laundered 20 times with Tide and Clorox at 140°F., followed by tumble drying. The untreated bras had a terrible, shrunken, distorted appearance after the first wash. The vapor phase treated sample, even after 20 repeated washes and dryings, showed no shrinkage, no signs of wear, no rips or tears, and still had a wash-and-wear rating of about 4.5 to 5.0 in various parts.

At the present time, 100% cotton brassieres and girdles cannot be treated by the resin, delayed cure process because the elastic components in the garments cannot tolerate the severe exposure of 10-20 minutes at 340-360°F. The vapor phase process offers an excellent opportunity to such garment manufacturers to produce durably pressed, washable, 100% cotton, high style undergarment materials.

100% Cotton Dresses

Two identical size, red colored (naphthol ?) cotton dresses were purchased. These had no finish and were doll sized. One was exposed for 4 hours at 50°C. as in the above case. When laundered 10 times with Tide at 140°F. and tumble dried, the untreated garment was badly distorted, especially in the lace collar portions. The vapor phase treated garment showed no shade changes, no shrinking, good shape retention, and a wash-and-wear rating of about 4.0. Of special importance was the fine shape retention of the cotton lace portions of the dress and the lack of abrasive wear during the washings.

100% Cotton Knitwear

Two 100% cotton boy's knit shirts were purchased. One was exposed as the bras described above. The treated and the untreated shirts were laundered together at 140°F. ten times and tumble dried. The vapor phase permanent press knit shirt had excellent appearance after the last wash and was not shrunken. The untreated garment was badly shrunken and distorted.

100% Cotton Shorts

Boy's cotton shorts were purchased and treated as above. In this case the vapor phase treatment produced a shade change in the blue color of the shorts. The dimensional stability and wash-wear performance of the vapor phase treated pair of shorts were very good. The untreated garment again shrank badly after 10 washes and was badly wrinkled after the last tumble drying.

100% Cotton Twill Pants

In order to study the degree of uniformity which could be produced in a garment containing multiple layers of cloth, the following was done: No. 413 cotton twill fabric was preimpregnated with 10% ethylene urea and dried. This fabric was then cut, sewn into miniature pants, steam pressed, and then crosslinked by exposure to Methyl Formcel-Formic Acid vapors as above. Another set was prepared from untreated cotton twill. This was also exposed in pants form to the vapor phase crosslinking agent. An untreated pair of pants from each set was retained. All four pants were laundered, with a 5-lb. load, twenty times at 140°F. with Tide and tumble dried after each wash. Both the ethylene urea pretreated and the non-pretreated pants, crosslinked in the vapor phase, had excellent shape retention and crease retention properties after the twenty washes. No signs of wear were evident! The untreated pants had shrunk and were badly wrinkled.

These garments were dyed with a direct dye, Fastusol Blue LBRR Conc. The untreated pants dyed a uniform dark navy blue. The vapor-phase crosslinked pants were uniformly immunized against direct dyeing. The ethylene urea preimpregnated fabric was less immunized than that crosslinked in a pure state. Examination of seams and the multilayers of cloth in the cuffs showed that the crosslinking had been uniform throughout the garments. These dyeing studies were encouraging for the practical utility of the vapor phase process in treating complex cotton garments.

General Comments on Cotton Garments

Although the garment treating studies have been few, and were confined to a small size or miniature single garment treatments, the results have been very encouraging in that some of the previous data on flat fabrics were confirmed: uniformity of treatment in single and multilayers of cotton; good to excellent wash-and-wear performance and crease retention; and improved wear resistance over conventional pad-dry-cure resin systems.

Vapor Phase Crosslinking

Permanent Press Requirements

In considering the concept of developing a practical vapor phase process for treating 100% cotton garments and to capitalize on the advantages produced therefrom, it was concluded that at least two basic variations were necessary:

1. For lightweight, soft white cotton items such as men's shirts, undergarments, knitwear, bed linen, blouses, and related garments, the vapor phase exposure to methanol hemiformal/formic acid mixture would produce a soft, permanent and completely chlorineproof finish.

2. For heavier fabrics such as men's slacks, dungarees, sport clothes, suits, corduroys, and others, it would be required to produce a full, firm hand in the permanent press garment. In this case, it would be necessary to treat the cotton fabric in the finishing plant with resin forming intermediates such as 5-15% of urea, ethylene urea, propylene urea, carbamic acid esters, monoureines, and the like. Moreover, other agents such as polyvinylacetate, water and oil repellants, acrylic lattices and other finishing agents might also be needed.

Urea preimpregnations, while economically suited for high weighting effects, were considered to be deficient from the point of view of durability and chlorine retention of the finish obtained. Consequently, most of the emphasis has been placed on preimpregnations with monoheterocyclic ureas and carbamic acid esters. These would produce both durable and chlorine resistant finishes after the vapor phase reaction.

With reference to both case No. 1 and No. 2 above, a further practical requirement is to reduce the reaction times in a vapor phase to about 15 minutes. While this could be done at high temperatures, it is preferred to try to accomplish the reaction at room temperatures to obtain the best value in high wear resistance. With chlorosilane exposures on DMEU preimpregnated fabrics, this has already been accomplished. Such a finish, however, is not suited for the garments in case No. 1 above, since the garments so produced are highly water repellent!